

GEOBAROMETRY, GEOTHERMOMETRY AND THE PROBLEM OF ZONING  
IN THE CASSITERITE-SULPHIDE DEPOSITS.

GEOBAROMETRY

Geological Considerations

The estimation of pressure from geological considerations can only be approximate due (a) to difficulties in applying accurate geological reconstructions and (b) to uncertainties as to whether the loads are lithostatic or hydrostatic. The maximum thicknesses of overburden above the deposits at the time of mineralization are calculated below from considerations discussed previously.

(a) Mt. Bischoff

The maximum thickness of rocks which could have been deposited above the dolomite horizon are:-

Siluro-Devonian	6000 feet
Ordovician	100 feet
Cambrian	18000 feet
Proterozoic - lower Cambrian	1000 feet
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Total	25100 feet

The thickness of approximately 25,000 feet may be far too high. The Cambrian sequence may be considerably reduced as Mt. Bischoff was probably a structural high during the Cambrian, and fossiliferous rocks similar to those of the Dundas Group (maximum thickness of

8900 feet in the Dundas area) have not been found in this area. It is also probable that mid-Devonian folding and uplift (Tabberabberan Orogeny) which preceded late Devonian granite intrusion was accompanied by severe erosion which reduced the thickness of the overburden present in Siluro-Devonian times (e.g. Solomon, 1962).

The maximum overburden of 25,000 feet is approximately equivalent to a lithostatic load of 1950 atmospheres and a hydrostatic load of 775 atmospheres.

(b) Cleveland

The maximum thickness of rock which could have been deposited above the ore horizon is less than at Mt. Bischoff. The Proterozoic-lower Cambrian rocks are below the ore horizon as are at least 5000 feet of Cambrian rocks if the ultramafic-mafic complex at Heazlewood is at the same stratigraphic level as the Serpentine Hill Complex in the Renison Bell area. The maximum overburden would therefore be 19,000 feet although a similar argument for a probable reduction of this thickness because of non-deposition of Dundas Group rocks and post-mid Devonian erosion applies as at Mt. Bischoff.

The maximum overburden of 19,000 feet is approximately equivalent to a lithostatic load of 1450 atmospheres and a hydrostatic load of 590 atmospheres.

(c) Renison Bell

The maximum thickness of rocks that could have been deposited above the ore horizons at Renison Bell is:

	Siluro-Devonian	6000 feet
	Ordovician	1500 feet
	Dundas Group	9000 feet
Cambrian	Crimson Creek Formation	8000 feet
Total		24500 feet

The maximum thickness is probably much closer to the actual overburden during mineralization than at Mt. Bischoff and Cleveland because the Cambrian sequences in particular have been more accurately delineated in this area although post - mid Devonian erosion very probably reduced the overburden. The maximum lithostatic and hydrostatic loads are similar to those at Mt. Bischoff.

The occurrence of tensional fractures prior to mineralization and of open spaces during ore deposition at Mt. Bischoff and probably at Renison Bell is not inconsistent with the estimated overburden. The lower limit of tensile failure for quartzite is approximately 10,000 feet (Secor, 1965) although quoted values of tensile strength vary considerably and do not allow an exact calculation. However Secor (1965) has shown that this limiting depth of tensile failure is a minimum which increases with increasing fluid pressure, and that this increase is significant for fluid pressure-overburden weight ratios such as those observed in deep oil wells. Secor (1965) has shown that open fractures can occur at depths of over 20,000 feet and may in fact represent earlier fractures which have been opened up by high fluid pressure at depth. This may have been an important process operating during intrusion of the acid rocks at Mt. Bischoff and Renison Bell.

### Fluid Inclusion Data

This section represents a joint project with Dr. Solomon.

If contemporaneous primary  $\text{CO}_2$  and aqueous inclusions can be identified in a mineral then it is possible to estimate the effective pressure using the density of  $\text{CO}_2$  (Holden, 1925; Roedder 1965; Koltun in Yesmakov, 1965).

Irregular, circular or tabular, two-phase  $\text{CO}_2$  inclusions occur in planar zones unrelated to fractures in fluorite from the Happy Valley Face at Mt. Bischoff (Plate 39). The  $\text{CO}_2$  was identified from the homogenization temperature of  $24^\circ\text{C}$  and its high thermal expansion coefficient. Duplicate analyses carried out by the Australian Microanalytical Service (C.S.I.R.O., Melbourne) on the fluorite from Happy Valley indicated the presence of a detectable amount of carbon (0.02%) ten times greater than that in a sample of fluorite (of equivalent weight) from the Slaughteryard Face, which had a carbon content close to the detection limit (0.002%).

In the larger  $\text{CO}_2$  inclusions a very small amount of aqueous solution (?) clings to pockets in the cavity walls. Aqueous inclusions from the same specimens, but occupying different zones, do not appear to contain  $\text{CO}_2$  but their small size makes identification of  $\text{CO}_2$  difficult.

Homogenisation temperatures for the Happy Valley primary aqueous inclusions (Fig. 29) range from  $156^\circ$  to  $170^\circ\text{C}$ , with five results averaging  $157^\circ\text{C}$  and one at  $170^\circ\text{C}$ . Salinity measurements (Fig. 28) on primary inclusions showed a range from 4 to 6 equivalent wt. per cent NaCl, with seven at 4% and two at 6%. Figure 27 shows the

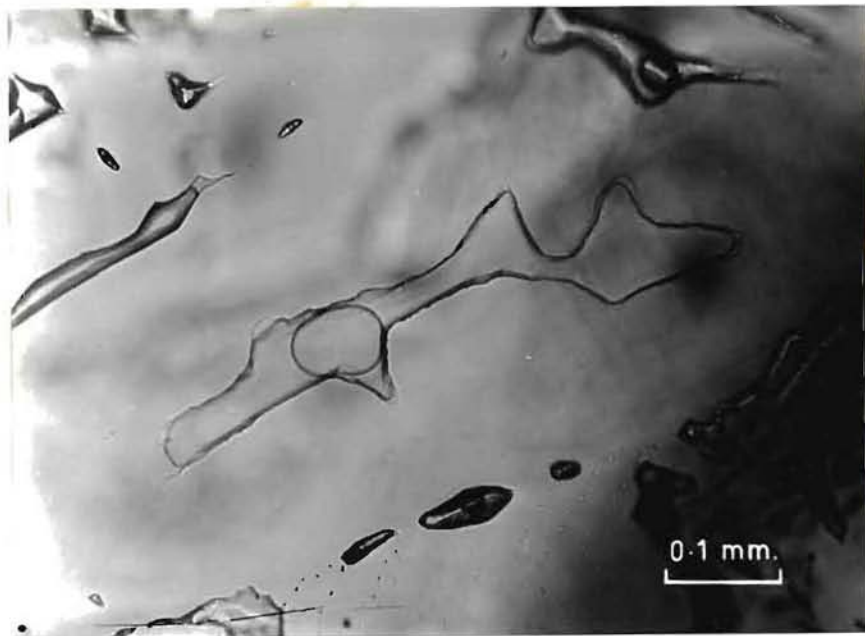


Plate 39 - Inclusions containing mainly liquid  $\text{CO}_2$  with a bubble of  $\text{CO}_2$  vapour and a small quantity of  $\text{H}_2\text{O}$  aqueous solution (?) in pockets along the walls of the inclusion, Happy Valley, Mt. Bischoff. Specimen No. 100839.

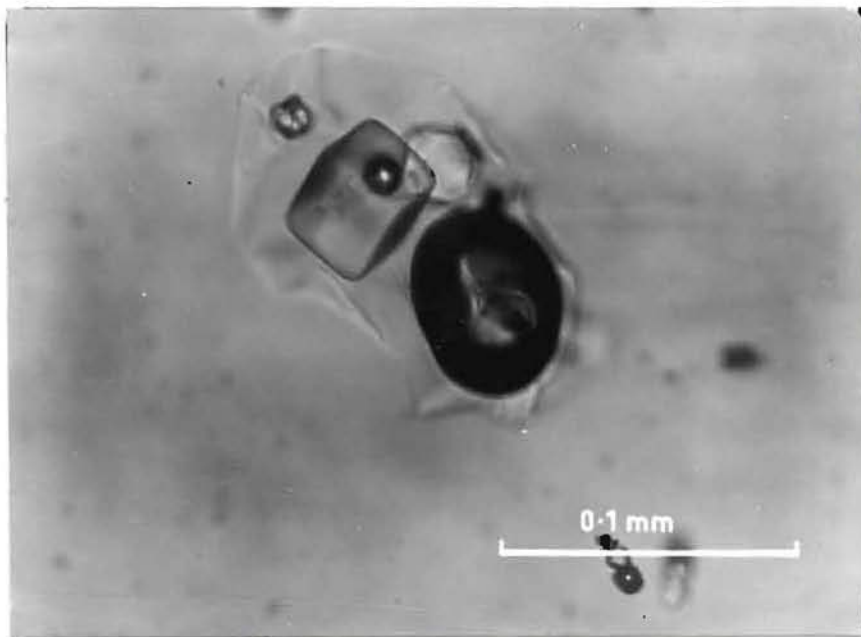


Plate 40 - Inclusion containing solid daughter minerals, probably halite and sylvite, Brown Face, Mt. Bischoff. Specimen No. 13511.

correction for pressure to be applied to these results, using lines of equal density derived from Klevstov and Lemmlein (1959), for pure water and solutions containing 10% NaCl and 20% NaCl by weight.

The density of the  $\text{CO}_2$  was determined by photographing the inclusions at  $10^\circ\text{C}$  and measuring the areal ratios of gas and liquid. Thirteen measurements were made on fairly regular inclusions and the densities obtained ranged from 0.67 to 0.73 g/cc with an average of 0.71 g/cc. The line corresponding to a constant density of 0.71 in Figure 27 is constructed from the P-V-T values of Kennedy (1954). If the aqueous and  $\text{CO}_2$  inclusions formed together, then the inclusions containing 6% NaCl apparently formed at about  $770 \pm 100$  atmospheres (allowing for the measured range in density) and the 4% NaCl inclusions at about  $760 \pm 100$  atmospheres.

These pressures are only approximate because the composition of the aqueous fluid is unknown and there could be minor impurities in the  $\text{CO}_2$ .

The question of whether the  $\text{CO}_2$  and aqueous inclusions formed at one time is clearly important. If the solution from which the fluorite was forming consisted mainly of NaCl,  $\text{H}_2\text{O}$  and  $\text{CO}_2$  at equilibrium, and was at  $210^\circ\text{C}$  and approximately 750 atmospheres, it should have consisted of two phases: NaCl- $\text{H}_2\text{O}$  with about 10%  $\text{CO}_2$  by weight in solution (Takenouchi and Kennedy, 1965) and  $\text{CO}_2$  with several per cent of NaCl- $\text{H}_2\text{O}$  in solution (Takenouchi and Kennedy, 1964). On cooling, two types of three-phase inclusions would have formed. Water was noted in the larger  $\text{CO}_2$  inclusions, and although the amount observed seems less than

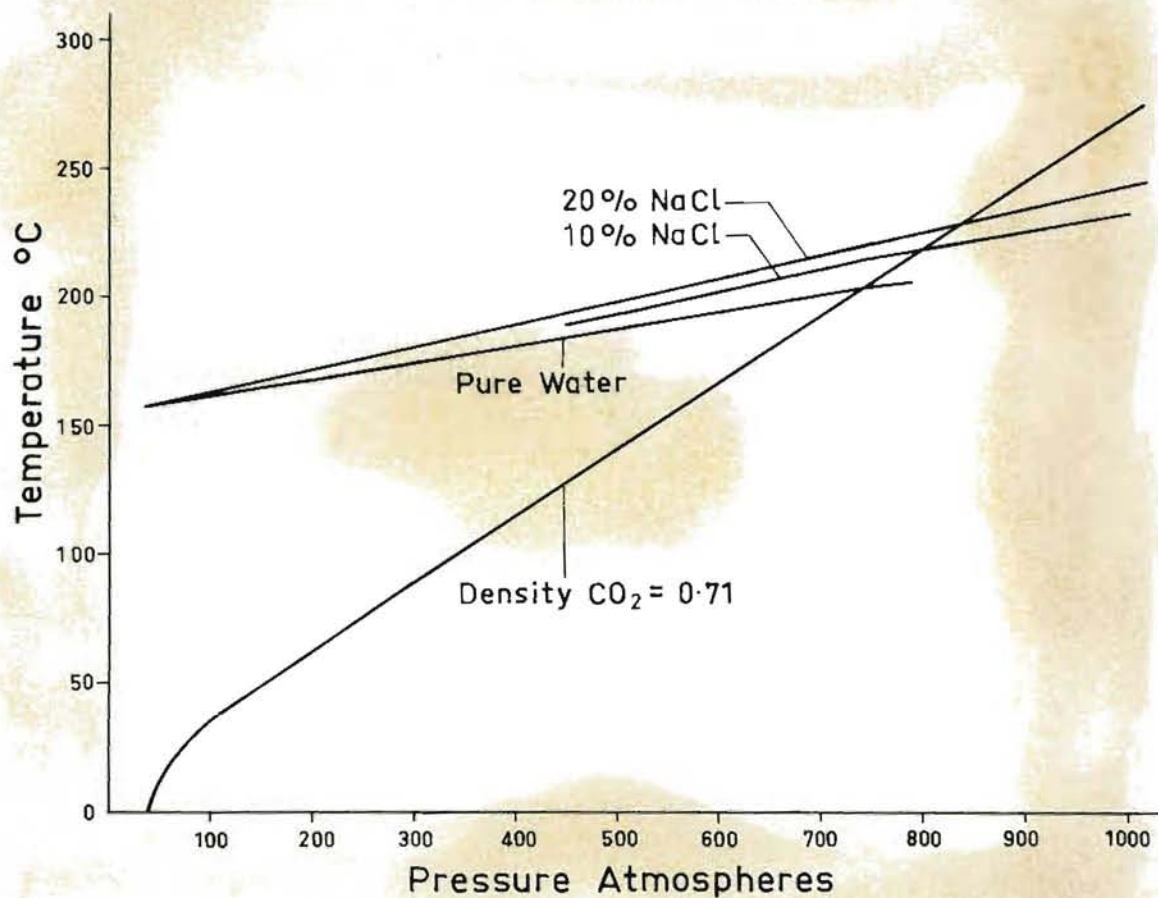


Figure 27. Lines of equal density for aqueous solution and CO<sub>2</sub> in terms of pressure and temperature, from data given by Klevstov and Lemmlein (1959) and Kennedy (1954).

10% by weight, there may be a very thin invisible film around the walls of the inclusions. The difficulties in observing  $\text{CO}_2$  in the aqueous inclusions are even greater. Hence it is difficult to test the observations against the experimental data. It is also possible that the experimental data may not strictly apply to the solutions present in the inclusions.

It is not clear whether the Happy Valley results can be applied throughout the area; presumably the pressure could vary for substantial periods between different fractures and ore zones.

One specimen (100,837) from Greisen Face contains coexisting liquid and gaseous inclusions that have a range of homogenization temperature from  $314^\circ$  to  $371^\circ\text{C}$  and from  $337^\circ$  to  $430^\circ\text{C}$  respectively (Fig. 29). The salinity of the inclusions is approximately equivalent to 10 wt. per cent NaCl. These inclusions do not appear to have developed by necking and it seems likely that the solutions were boiling, indicating a low confining pressure of approximately 100 atmospheres. The low pressure zone must have been extremely local as no other coexisting liquid and gaseous inclusions have been identified.

If the figure of 750 atmospheres is accepted as the prevailing pressure it could be greater than, equal to, or less than the overburden pressure. At Mt. Bischoff the figure calculated for the  $\text{CO}_2$  density is approximately equal to the maximum hydrostatic load (775 atmospheres). The overburden would have to be reduced to 10,000 feet by the late Devonian for the calculated pressure to approach a lithostatic load. It is probable that the pressure was largely intermediate between the hydrostatic and lithostatic extremes.



## GEOOTHERMOMETRY AND ZONING

### Introduction

Several authors (e.g. Park, 1955) have drawn attention to the parallelism which might be expected between zonal sequence and paragenetic sequence in an idealized hydrothermal vein system, and Both and Williams (1968) have recently summarised many of the features of hydrothermal zoning.

A high probability that the cassiterite-sulphide deposits and surrounding Pb-Zn-Ag fissure deposits belong essentially to the same phase of mineralization in a common metallogenic province has been demonstrated. The cassiterite-sulphide deposits are considered to have been deposited at an initially higher temperature because the earliest formed minerals (e.g. cassiterite, wolframite, arsenopyrite, tourmaline, topaz) are virtually restricted to these deposits (Groves and Solomon, 1964). The Pb-Zn-Ag deposits contain minerals of intermediate or late position in paragenesis (e.g. sphalerite, galena, jamesonite). A major exception to this general trend is that pyrite which has been deposited before pyrrhotite is more abundant in the Pb-Zn-Ag deposits while pyrrhotite is the predominant sulphide of the cassiterite-sulphide deposits.

At Mt. Bischoff lateral mineralogical zoning can be demonstrated on a local scale. The replacement deposit in the central area of the mine (e.g. Brown Face, Slaughteryard Face) consists of massive pyrrhotite with cassiterite, arsenopyrite, pyrite and wolframite with extremely rare sphalerite and no galena or jamesonite. Further south (e.g. Greisen

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Face, Pig Flat) pyrite, sphalerite, galena and jamesonite become more abundant although pyrrhotite is still predominant, and in the south end of the open cut and Happy Valley Face pyrite is predominant with sphalerite and some galena in largely unmineralized dolomite. The surrounding fissure veins (e.g. Giblin and North Valley Lodes) contain cassiterite with predominantly pyrite and common sphalerite, galena and jamesonite for a radius of 3,000 feet from Mt. Bischoff Peak, and outside this area they contain predominantly galena and sphalerite with jamesonite (e.g. Silver Cliffs, Magnet). Fook's Lode which is approximately 5,000 feet SE of Mt. Bischoff Peak (Fig. 8) is unusual in that it is similar to the vein deposits within the inner circular area. Mineralogical zoning has also been recorded within the fissure veins, Weston-Dunn (1922) recording abundant cassiterite and wolframite and rare galena in the Giblin Lode near the summit of Mt. Bischoff and abundant sphalerite, galena and jamesonite towards its SW extremity.

The mineralogical zoning at Mt. Bischoff has been attributed, at least in part, to the existence of a temperature gradient from the centre of Mt. Bischoff outwards (Groves and Solomon, 1964), and it is evident that similar gradients may exist at Renison Bell and Cleveland.

In this section an attempt has been made to quantify the temperature and other parameter variations at Mt. Bischoff using fluid inclusion data and sulphide systems, and to correlate these with data from the Renison Bell and Cleveland ores. Unfortunately no suitable material was available for fluid inclusion studies at Renison Bell and Cleveland and even the scope of the investigation at Mt. Bischoff has been partly

restricted by the comparatively rare occurrence of suitable minerals, and by their occurrence commonly late in paragenesis.

Fluid Inclusion Studies at Mt. Bischoff

(a) Nature of the Inclusions

Fluorite and quartz from the Mt. Bischoff mine contain numerous, generally two-phase aqueous inclusions; the maximum size being 0.2 mm x 0.04 mm. The inclusions vary considerably in shape, common forms being ovoid, wedge, tubular, reticulate and club-shaped. Necked and partially necked inclusions can be recognized in some specimens (Plate 42). Some inclusions are small, irregular and poorly-defined and occur in planar surfaces related to fractures. These have been grouped as secondary inclusions. More regular (commonly spherical), well defined inclusions of variable size that occur in surfaces unrelated to fractures (Plates 43 and 44) and well defined, large inclusions of variable shape that occur singly (Plate 41) or in non-planar groups have been interpreted as primary inclusions. The distinction between primary and secondary inclusions is commonly difficult, particularly when they are small. The identification of pseudo-secondary inclusions (e.g. Yermakov, 1965) proved impracticable because of the poor development of crystal faces.

Inclusions containing a solid phase are rare. Negative crystals in fluorite from Fook's Lode contain clear liquid and a bubble with single or grouped acicular crystals of a dark green, anisotropic mineral with straight extinction, which may be tourmaline.

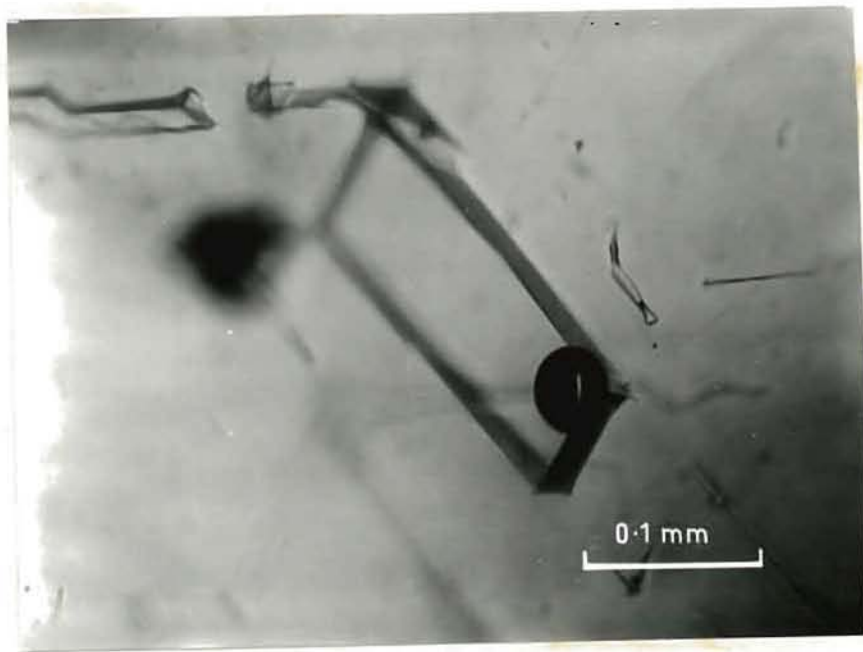


Plate 41 - Negative crystal in fluorite filled with aqueous solution and vapour bubble, Pig Flat, Mt. Bischoff. Specimen No. 100838.

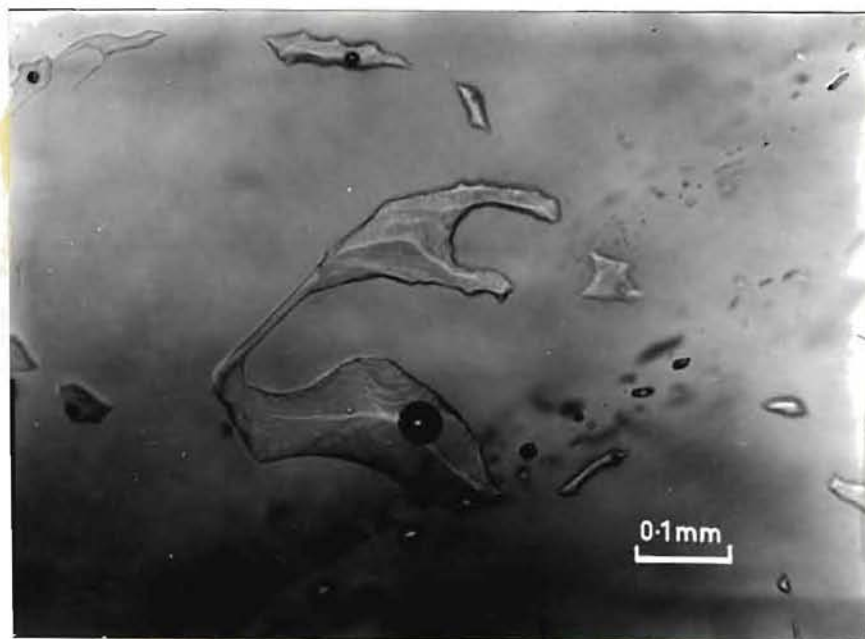


Plate 42 - Partially necked inclusion in fluorite, Pig Flat, Mt. Bischoff. Specimen No. 100838.

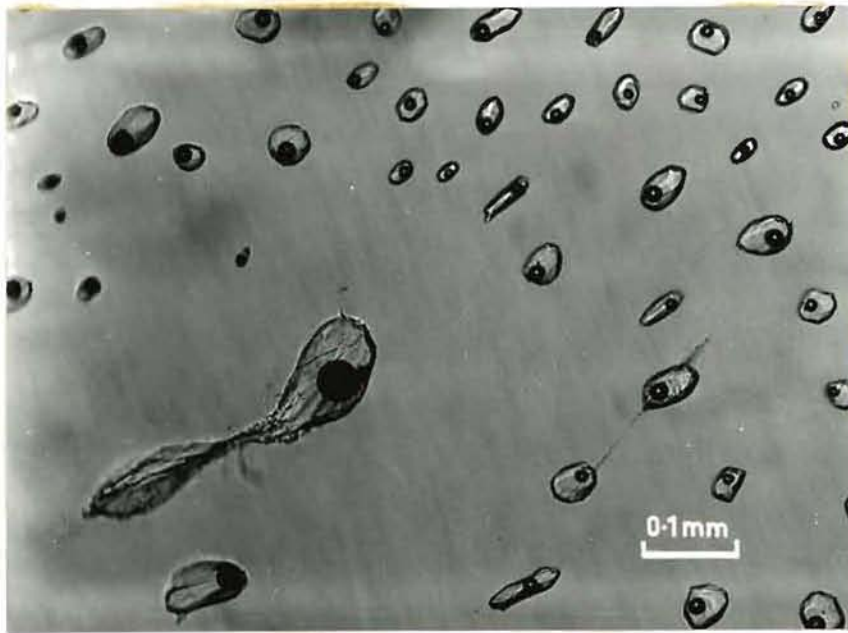


Plate 43 - Inclusions occupying a planar surface in fluorite, Slaughteryard Face, Mt. Bischoff, Specimen No. 100, 025.

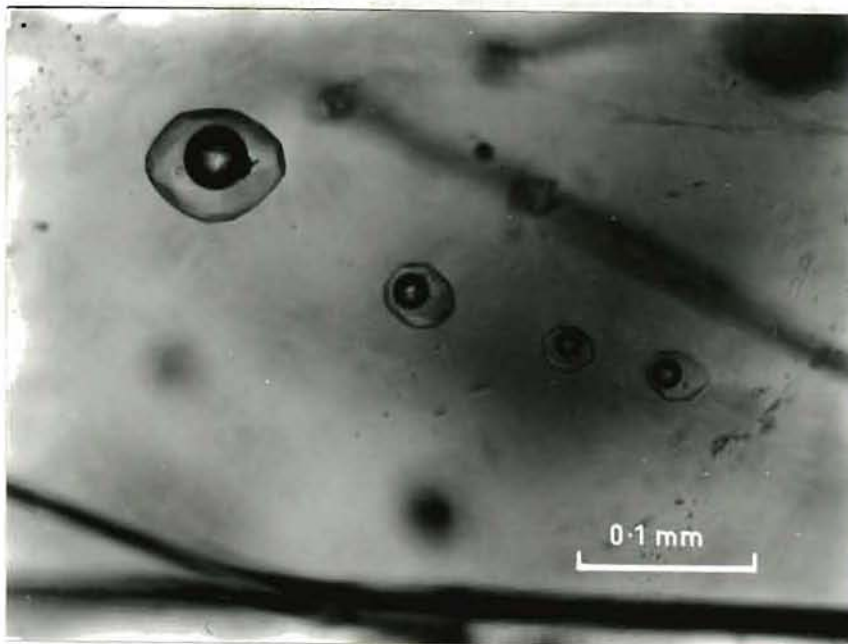


Plate 44 - Aqueous inclusions with high vapour bubble/liquid ratios in fluorite, Fook's Lode, Waratah. Specimen No. 100, 206.

Larger needles of tourmaline are common in the fluorite and in one example the needle passes through four inclusions. Multi-phase inclusions up to 0.8 mm in length occur in fluorite from the Brown Face. They consist of up to 30 per cent by volume of solid daughter minerals which are largely cubic, with other minor phases including possible sulphides (Plate 40). The smaller cubic crystals generally dissolve at about 75°C, and the larger, well-formed cubic crystals dissolve at temperatures of up to 340°C. These may be sylvite and halite respectively. Little (1960) has also recorded "salt" crystals in inclusions in cassiterite from Mt. Bischoff.

Inclusions containing CO<sub>2</sub> from Happy Valley Face have been described above. A few three-phase H<sub>2</sub>O-CO<sub>2</sub> inclusions (aqueous solution, liquid CO<sub>2</sub> and gaseous CO<sub>2</sub>) have been found in fluorite from Slaughteryard Face and some very irregular, small, two-phase CO<sub>2</sub> inclusions in fluorite from Fook's Lode.

#### (b) Salinity Data

For determinations of salinity by the melting point method, the sections were pre-frozen in dry ice to avoid the effects of super-cooling (Roedder, 1962). They were transferred to a stage immersed in acetone and dry ice, at a temperature of about -25°C. The temperature of the system was allowed to gradually increase and the temperatures at which the last ice crystal in an inclusion melted were recorded. These melting points have been interpreted in terms of the system NaCl-H<sub>2</sub>O (Fig. 28).

Figure 28. Frequency distribution of melting point determinations on inclusions carrying aqueous solutions, combined with salinity estimates expressed as weight per cent NaCl, based on data given by Stephen and Stephen (1963). Inclusions in fluorite and quartz from Mt. Bischoff area. S = secondary inclusions.

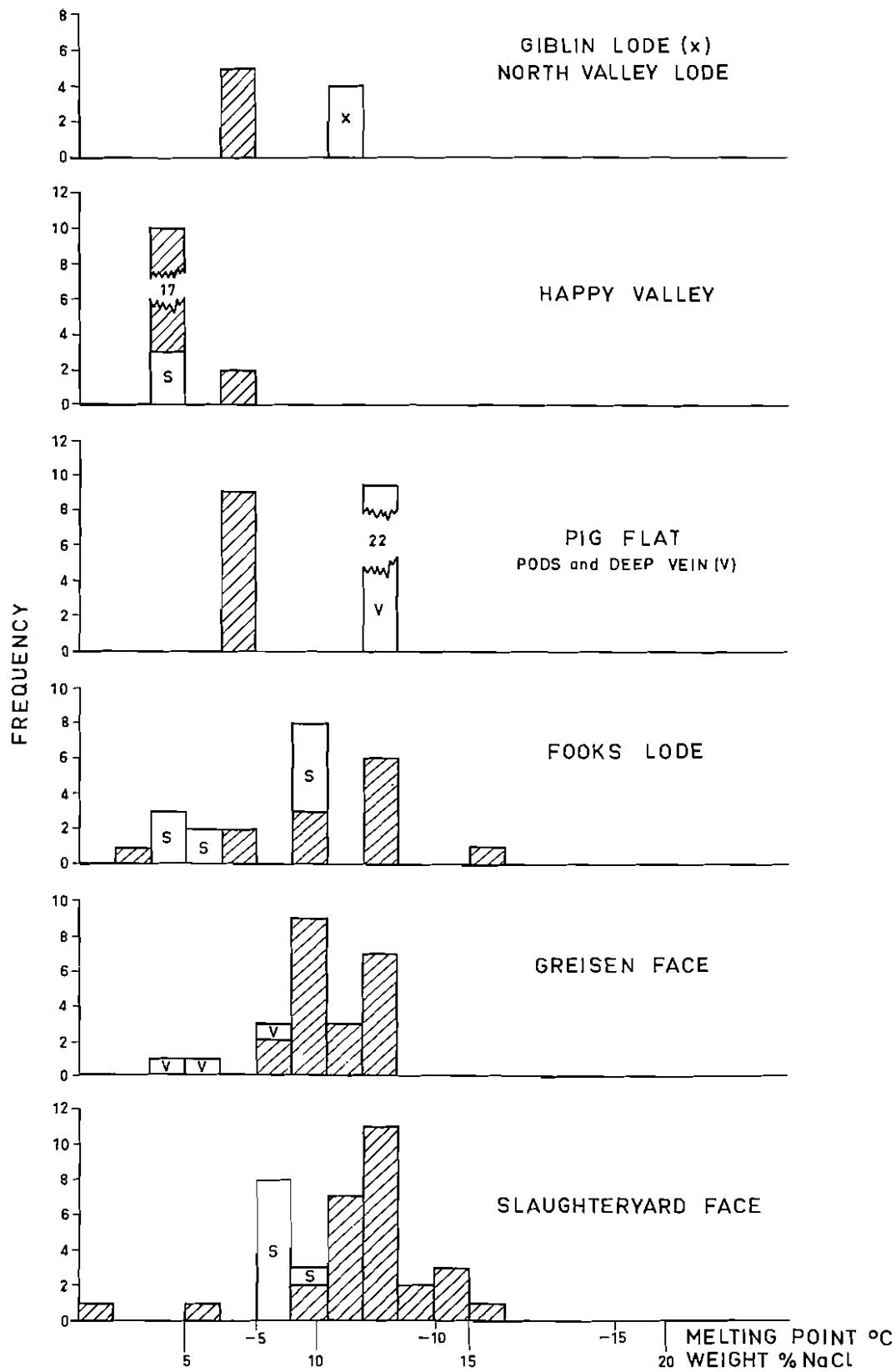


Figure 28



The salinities are accurate to  $\pm 1$  equivalent wt. per cent NaCl. The salinity of inclusions from the Brown Face (13511) cannot be directly measured but is probably greater than 50 equivalent wt. per cent NaCl as the inclusions contain up to 30 per cent by volume of NaCl and KCl crystals.

The marked variation of salinity within inclusions from a single locality is apparently a common feature of ore deposits (e.g. Sawkins, 1966b). The variation may be accentuated by inaccuracies involved in the expression of salinity as equivalent wt. per cent NaCl, instead of a more realistic ratio of NaCl and KCl, but cannot be fully explained by it. Consistency of K/Na ratios in bulk samples (Table 8) need not necessarily indicate consistency of composition between individual inclusions. Rapid changes in salinity in one area may result from rapid changes in salinity of the hydrothermal solutions (e.g. Sawkins, 1966b), localised boiling or pulsating incursion of hydrothermal waters into rocks containing meteoric and connate waters. It is possible that highly saline inclusions such as those in the Brown Face fluorite are the result of local boiling and are not representative of the original hydrothermal solution.

#### (c) Temperature Data

The filling temperatures of inclusions (Table 7, Fig. 29) were measured on a heating stage similar to that used by Sawkins (1964). The heating rate was maintained at approximately  $2^{\circ}\text{C}$  per minute and the filling temperature measurements were accurate to within  $\pm 2^{\circ}\text{C}$ .

Figure 29. Frequency distribution of filling  
temperatures of inclusions in fluorite  
and quartz from Mt. Bischoff area.

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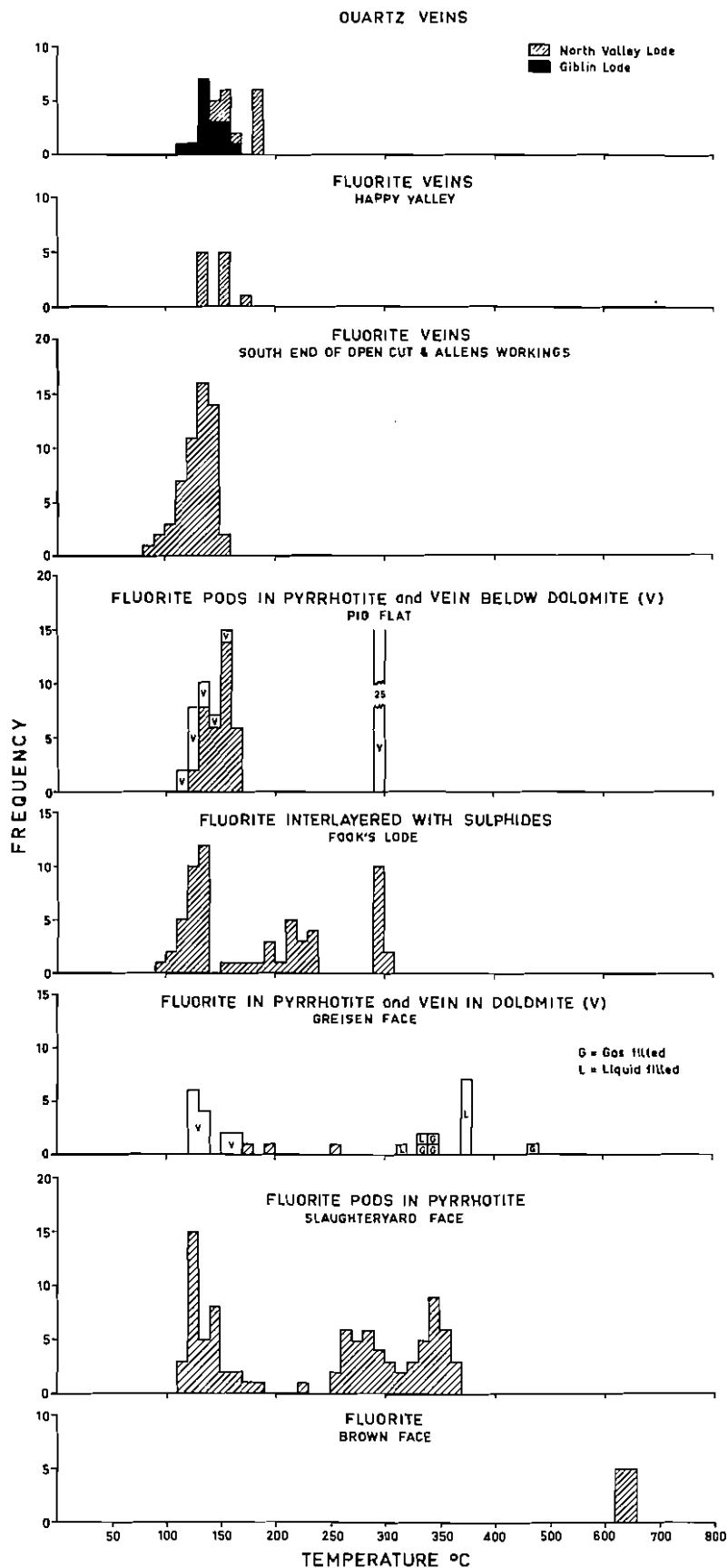


Figure 29

It is apparent that there are wide ranges of filling temperatures for each locality; these ranges are far wider than for individual specimens for which the range is generally less than  $20^{\circ}\text{C}$  to  $30^{\circ}\text{C}$ , in agreement with other studies (e.g. Sawkins, 1966b). The one notable exception is from a fluorite vein beneath the dolomite near Pig Flat, where the filling temperatures for primary and secondary inclusions in one fragment ranged from  $112^{\circ}$  to  $150^{\circ}\text{C}$  but 25 inclusions in a single plane gave temperatures between  $295^{\circ}$  and  $298^{\circ}\text{C}$ . It was generally found that the primary inclusions occurring in surfaces unrelated to fractures have slightly higher filling temperatures than single primary inclusions in the same specimens. The filling temperatures for inclusions from the Slaughteryard Face and Fook's Lode show a bimodal distribution (Fig. 29), the lower temperature groups consisting of the visually defined secondary inclusions and the higher temperature groups the primary inclusions. The secondary inclusions from fluorite and quartz throughout the mine area have a range of filling temperatures from about  $90^{\circ}\text{C}$  to  $260^{\circ}\text{C}$ , the majority occurring between  $120^{\circ}\text{C}$  and  $150^{\circ}\text{C}$ . The ranges of filling temperatures of poorly defined primary and secondary inclusions overlap in fluorite patches from Pig Flat, fluorite veins from the south end of the open cut and Greisen Face and quartz veins from Giblin Lode, and have been grouped together in Table 7. The overlapping ranges have resulted in a negatively skewed, unimodal distribution for filling temperatures of inclusions from fluorite veins at the south end of the open cut (Fig. 29).

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In a general study of inclusions from tin deposits, Little (1960) obtained the following results for Mt. Bischoff samples (locality unknown): in cassiterite and tourmaline primary inclusions filled at 300°C, and in quartz the primary inclusions filled at 394-416°C (four measurements) and the secondary (?) inclusions filled at 248-268°C (five measurements).

The filling temperatures of the primary inclusions can be used in the determination of the formation temperatures of the host minerals provided several basic assumptions can be satisfied. The validity of these assumptions has been argued at length (e.g. Ingerson, 1947; Kennedy, 1950; Bailey and Cameron, 1951; Skinner, 1953; Roedder, 1960a), but recent geologically controlled, detailed studies (e.g. Roedder, 1960b; Schmidt, 1962; Hall and Friedman, 1962; Sawkins, 1962; 1966a) have given consistent results which appear to support the validity of the assumptions.

Salinity and pressure corrections have been applied to the filling temperatures (Table 7) using the experimentally derived curves of Klevstov and Lemmlein (1959). The maximum ranges of temperature were determined from the extreme values of salinity and pressure, as in some cases it was impossible to measure the salinity of every inclusion for which a corresponding filling temperature was determined. Average temperatures of formation were obtained from the average filling temperature using the average salinity of inclusions from equivalent samples and a pressure of 750 atmospheres. The uncertainty in distinction between secondary and primary inclusions in specimens from the south end of

Sample No. (No. of Samples)	Locality	Description	No. Measured	Range of filling temp. (°C) for secondary inclusions	Range of filling temp. (°C) for primary inclusions	Max. range (°C) for primary inclusions (press. & salinity corrected)	Average Corr. temp. primary inclusions
13511 (2)	Brown Face	Pale green fluorite association unknown	10	-	513 - 529 (519)	570 - 590 (?)	580 (?)
100204 100205 (20)	Slaughteryard Face	Colourless to pale pink fluorite:- pods in pyrrhotite	92	110 - 190	220 - 370 (302)	285 - 470	370
100837 (1)	Greisen Face	Colourless to pale pink fluorite:- pods in pyrrhotite	18	175 - 256	230 - 430 (352)	296 - 430	355
100826 (1)	Greisen Face	Colourless to pink fluorite:- vein in dolomite	14	125 - 162 (136)		185 - 220 (?)	195 (?)
100206 (12)	Fook's Lode	Colourless to green fluorite interlayered with sphalerite and cassiterite	62	90 - 140	151 - 303 (221)	210 - 380	290
100838 (4)	Pig Flat	Colourless to pink fluorite:- patches in pyrrhotite	37	125 - 168 (147)		185 - 230 (?)	210 (?)
100771 (1)	South of Pig Flat in drill hole.	Colourless to green fluorite :- vein in shales below dolomite	37	112 - 150	125 - 298 (280)	180 - 370	350
13526 13527 (14)	South end of open cut	Colourless to pink fluorite:- veins in dolomite	55	105 - 171 (157)		165 - 230 (?)	220 (?)
100839	Happy Valley	Pale pink fluorite:- veins in dolomite	11	132 - 138	156 - 170 (159)	215 - 230	220
100222 (4)	North Valley Lode	Colourless to smokey quartz associated with cassiterite	12	132 - 152	180 - 186 (183)	240 - 250	245
100223 (2)	Giblin Lode	Colourless to smokey quartz associated with cassiterite	18	115 - 165 (141)		170 - 220 (?)	200 (?)

Table 1. Filling temperatures and corrected temperatures from fluid inclusions in fluorite and quartz, Mt. Bischoff.

the open cut, the vein in Greisen Face, and the Giblin Lode may mean that the corrected filling temperatures given in Table 7 are lower than the true values for the primary inclusions alone. No correction has to be applied to inclusions in fluorite pods from Greisen Face because the coexistence of liquid and gaseous inclusions indicates a two-phase condition.

The corrected filling temperatures, equivalent to the formation temperatures of the host minerals, can only be interpreted if both the factors of spatial distribution and time of deposition are considered.

The fluorites from the Slaughteryard Face, Greisen Face, Pig Flat and Fook's Lode occur in pods that appear to be more or less contemporaneous with the pyrrhotite and have been veined by chalcopyrite. The fluorites from the Greisen Face (vein), south end of the open cut and Happy Valley occur in veins which cut altered dolomite and may be representative of a later stage of deposition. The Giblin and North Valley Lodes are demonstrably a later phase of mineralization than the replacement ore body. The mode of occurrence of the fluorite from Brown Face is unknown but it is likely to be similar to that in Slaughteryard Face.

The "early" fluorite shows a general decrease in average temperature of formation from Brown Face ( $580^{\circ}\text{C}$ ), Slaughteryard Face ( $370^{\circ}\text{C}$ ), Greisen Face ( $355^{\circ}\text{C}$ ) to Pig Flat ( $210^{\circ}\text{C}$ ). It is possible that the high temperatures obtained from inclusions in Brown Face fluorite may be fortuitous due to mechanical trapping of a gaseous phase during boiling, but the consistency of the filling temperatures suggests that they are probably real temperatures. The fluorite

from Fook's Lode has an anomalously high average temperature of formation ( $290^{\circ}\text{C}$ ). The average temperature of formation of possible late-stage fluorite from the south end of the open cut and Happy Valley ( $210$ - $220^{\circ}\text{C}$ ) is equivalent to that of "early" fluorite from the same area, and is similar to temperatures of formation of quartz associated with cassiterite in fissure veins. An exception is provided by an isolated fluorite vein in shales 200 feet beneath the dolomite horizon just south of Pig Flat, from which one group of inclusions gave a significantly higher temperature than other inclusions in the same specimen and from the same area (Fig. 29). This may be related to the greater depth of occurrence. In general it appears that there was a high temperature zone in the central area of Mt. Bischoff with a generalized decline in temperature outwards during replacement of the dolomite horizon, and that subsequent deposition of fluorite and quartz in predominantly marginal fissure veins occurred within the same temperature range as deposition of fluorite in the marginal zone of the replacement deposit. Fook's Lode may represent a local high temperature area, possibly associated with adjacent quartz-porphyry dykes in Falls Creek (Figs. 6 and 8).

Roedder (1960b) has shown a sympathetic decrease in filling temperature and salinity in zoned sphalerite crystals. A correlation between temperature and salinity in other more general studies has been impeded by the erratic local distribution of salinity in inclusions. In this study a plot of average temperature of formation against average salinity of fluid for each set of spatially controlled specimens (Fig. 30) indicates a



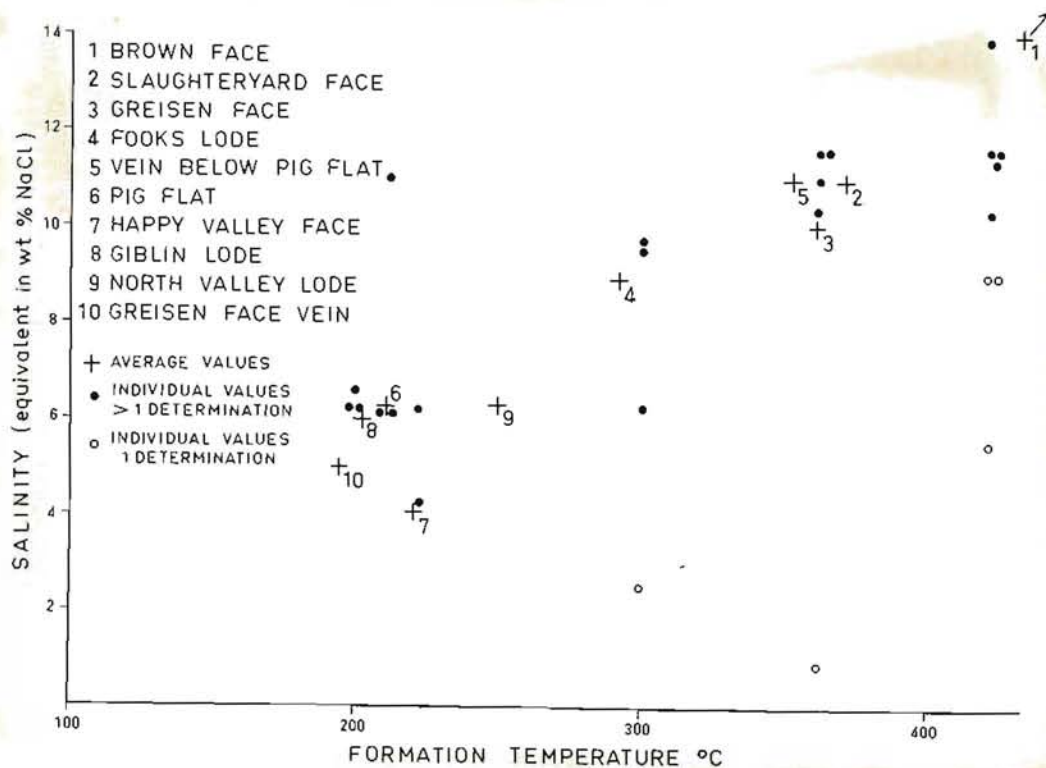


Figure 30. Plot of salinity v. temperature of formation using average values of primary inclusions and values for individual primary inclusions for which both parameters were measured.

generalized positive correlation between temperature and salinity (correlation coefficient,  $r=+0.76$ ). This correlation is confirmed by a plot of individual primary inclusions for which both temperature and salinity were measured ( $r=+0.81$ ).

A possible mechanism causing a decrease in both temperature and salinity of the ore solutions together with considerable local variation is localized, irregular mixing of a hot, saline, hydrothermal solution with cooler, less saline meteoric and connate waters. If the meteoric and connate water contained about 2% NaCl (White, Hem and Waring, 1963), dilutions of the hydrothermal solutions by up to 6 times the volume of meteoric and connate water would be required to lower the salinity from 14 to 4 equiv. wt. % NaCl. A further cause of declining temperature is loss of heat from the hydrothermal solutions to the wall rocks.

(d) Alkali Ratio Data

Previous workers (e.g. Yermakov, 1965; Roedder et al 1963) have shown that the majority of aqueous solutions in fluid inclusions contain predominantly dissolved alkali salts and minor Ca and Mg salts (chlorides and sulphates). The occurrence of multi-phase inclusions containing probable halite and sylvite from Mt. Bischoff suggests that the solutions in inclusions from this deposit are similar to those described elsewhere.

Absolute ionic concentrations could not be measured from the small inclusions present at Mt. Bischoff, but it was possible to determine the ratios of Na, K and Li, using methods outlined by Sawkins (1966a). Care was taken to reduce contamination by selecting clean fragments,

and about 25 grams of each sample was crushed in a vibratory swing mill for 3 seconds. The powdered sample was weighed into a polythene, screwtop jar and leached with half its weight of deionized water. The liquid was then filtered and analysed for Na, K and Li by flame photometry. Specimens of quartz and fluorite from the Rookhope borehole (Table 8) gave weight ratios comparable to those quoted by Sawkins (1966a).

These studies were limited by the lack of suitable quantities of clean material from several areas and have the disadvantage that secondary, and primary inclusions cannot be analysed separately. From the few ratios available it appears that the marginal lode deposits have higher Na/K weight ratios than the high-temperature pyrrhotite ores. Fook's Lode fluorite, despite its high filling temperatures and salinities, has a similar ratio to the lode deposits.

In general, the Na/K and Na/Li ratios are similar to those for fluids from volcanic areas such as the "acid sulphate-chloride waters" (White, Hem and Waring, 1963).

Roedder (1958) recorded similar Na/K ratios in gold-quartz veins from California and Sawkins (1966b) obtained Na/K ratios as low as 2.8 for inclusions in Cornish tin deposits. The Salton Sea brines have similar ratios and although originally considered to be magmatic (White, Anderson and Grubbs, 1963) they are now considered to be meteoric on the basis of isotopic composition (Craig, 1966). The Na/K ratio in these fluids is probably derived by leaching from sediments. White (1965) showed that there is a general decrease in the Na/K ratio with increasing temperature for hot spring waters in equilibrium with alkali feldspars and K-mica,

Mineral	Number	Locality	Na/K	K/Na	Li/Na
Fluorite	13511	Brown Face	1.12	0.89	0.0210
"	100204 (a)	Slaughter-yard Face	1.44	0.70	0.0077
"	100204 (b)	"	1.41	0.71	0.0129
"	100205 (a)	"	1.37	0.73	-
"	100205	"	1.12	0.90	0.0313
"	100206	Fook's Lode	3.36	0.30	0.0117
Quartz	100223	Giblin Lode	2.62	0.38	0.0105
"	100222	North Valley Lode	4.03	0.25	0.0120
Green Fluorite		Rookhope, U.K.	5.60	0.18	0.0035
Purple Fluorite		Illinois, U.S.A.	6.51	0.15	0.0004
Quartz		Rookhope U.K.	5.86	0.17	0.0027
Ocean Water (1)			27.8	0.036	0.00001
Salton Sea (2)		California, U.S.A.	2.0	0.50	0.0059

Table 8. Alkali weight ratios of fluid inclusions from Mt. Bischoff and other occurrences.

Figures for (1) and (2) are from White (1965) (Table 1).

and that this is consistent with experimentally determined compositions of fluids in equilibrium with these minerals. The Na/K ratios and filling temperatures of inclusions from Mt. Bischoff consistently fall above the curves given by White (1965, p. 259), in agreement with parameters for waters that are not in equilibrium with alkali feldspars and K-micas.

Obvious sources of K and Li at Mt. Bischoff are the unaltered porphyry dykes which contain (Appendix A4, Table 26) from 2.25 and 5.0%K (average 4.05%) 0.08 to 0.45% Na (average 0.19%) and 45 to 190 ppm Li (average 103 ppm). Following alteration they contain from 0.08 to 0.33%K (average 0.12%), 0.01 to 0.04% Na (average 0.02%) and 5 to 27 ppm Li (average 9 ppm). The low Na/K and Na/Li ratios are therefore probably a function of relative availability of the alkalies with excess K and Li derived from the altered porphyry dykes by a hydrothermal fluid which was not in equilibrium with the dyke rocks.

The increase in Na/K ratios with falling temperature and salinity may be explained by mixing with meteoric and connate waters. The dilution required to explain the variation in salinity, would change an initial Na/K ratio of 1.3 to a final ratio of 3, which is approximately the change observed. The tendency of K to become fixed the micaceous minerals may also lead to relative concentration of Na. Addition of K to the dolomite host rocks is indicated by the presence of phlogopite in the gangue.

The anomalous high Na/K ratios of inclusions from Fook's Lode may be explained in terms of initial availability of the alkalies if a local source is envisaged.

(e) Summary and Conclusions.

Formation temperatures of fluorite and quartz support the concept of a generalized temperature decline outwards from the centre of Mt. Bischoff, as previously indicated by variation in the mineralogy of the sulphides. Initial temperatures of deposition of fluorite in the Brown Face were as high as  $580^{\circ}\text{C}$  and decreased to approximately  $200^{\circ}\text{C}$  in the marginal zone some 2000 feet away. Temperatures of formation of fluorite and quartz in later marginal fissure veins range from  $170^{\circ}$  to  $380^{\circ}\text{C}$ , with the majority between  $200^{\circ}\text{C}$  and  $250^{\circ}\text{C}$ .

A positive correlation exists between salinity and temperature of formation for minerals from different localities. A possible mechanism to explain (a) this correlation (b) the great variation of salinity within one area (c) the temperature decline and (d) the high salinities of inclusions from the Brown Face is for initially hot, highly saline hydrothermal solutions to be mixed with cooler, less saline meteoric and connate waters, in conjunction with heat loss from the solutions to the wall rocks. The occurrence of meteoric and connate waters at depths of over 10,000 feet is possible (e.g. White, 1968), particularly in an environment with open fractures and carbonate beds.

Low Na/K and Na/Li ratios of fluid inclusions from Brown Face and Slaughteryard Face probably result from addition of excess K and Li over Na from hydrothermal alteration of the porphyry dykes which may have been feeders to the mineralization. The Na/K ratio of the ore solutions increased with declining temperature and salinity possibly due to admixing with relatively Na-rich meteoric and connate waters; this increase may have been accentuated by fixation of K in micaceous minerals (e.g. phlogopite). A possible local source of solutions is indicated for deposition of fluorite at Fook's Lode which has a relatively high temperature of formation and salinity but similar Na/K ratios to the other marginal deposits.

## Temperature Indications from Sulphide Systems

### (a) The Fe-S System

The determination of pyrrhotite compositions is described in Appendix C2 and results are tabulated in Appendix C2, Tables 39 and 40. The composition of monoclinic pyrrhotites was not determined directly for reasons discussed in Appendix C2 but several authors have shown a restricted range of composition from 46.4 to 46.8 atomic percent Fe (e.g. Clark, 1966).

Arnold (1957) showed that the composition of pyrrhotite formed in equilibrium with pyrite was a function of temperature between 325° and 600°C. More recently Toulmin and Barton (1964) have shown that the composition of pyrrhotite is a function of both temperature and fugacity of sulphur ( $f_{S_2}$ ) and that the composition of pyrrhotite at a given temperature uniquely fixes the  $f_{S_2}$  and the activity of FeS ( $a_{FeS}$ ). They have shown that the temperature and  $f_{S_2}$  conditions of formation of pyrrhotite of a certain composition are a minimum when that pyrrhotite is formed in equilibrium with pyrite (Fig. 31). Von Gehlen and Kullerød (1962) have shown that the presence of chalcopyrite may lead to an even lower estimate of temperature but that the presence of sphalerite or galena has negligible effect.

The mode of formation of the monoclinic pyrrhotite must be known before any thermometric significance can be attached to its composition, because it has been shown by numerous authors that monoclinic pyrrhotite is a stable form only below the  $\beta$  transformation at about 300°C (e.g. Grønvold and Haraldsen, 1952; Desborough and Carpenter, 1965; Clark, 1966).

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Desborough and Carpenter (1965) have suggested the following possible origins for monoclinic pyrrhotite.

- (a) Extremely rapid isochemical cooling of hexagonal (2A, 7C) pyrrhotite with the composition of the resultant monoclinic pyrrhotite, which could revert to the monoclinic form without exsolution of pyrite. The original hexagonal pyrrhotite would be in equilibrium with pyrite between about  $450^{\circ}$  and  $525^{\circ}\text{C}$  (Fig. 31).
- (b) Extremely slow cooling of similar hexagonal (2A, 7C) pyrrhotite down the pyrite-pyrrhotite solvus with exsolution of pyrite and sympathetic increase in Fe content of the pyrrhotite down to the transformation temperature where the pyrrhotite would invert to the monoclinic form.
- (c) Oxidation of pyrrhotite with magnetite formed at the expense of pyrrhotite.
- (d) Hydrothermal modification of pyrrhotite by later sulphide-rich solutions (e.g. associated with the formation of secondary pyrite).
- (e) Direct formation of monoclinic pyrrhotite.

The lack of exsolved pyrite in the monoclinic pyrrhotite suggests that very rapid or slow cooling of S-rich hexagonal pyrrhotite are possible mechanisms for the formation of monoclinic pyrrhotite. An extremely slow cooling history appears the more reasonable geologically. An oxidation origin for the monoclinic pyrrhotite is unlikely because of the general lack of magnetite. Hydrothermal modification by sulphide-rich phases is possible at Mt. Bischoff because of the presence of second generation, hypogene pyrite replacing pyrrhotite.

However, many specimens of monoclinic pyrrhotite contain no second generation pyrite and it is absent or rare at Cleveland and the Federal Lode (Renison Bell) where the pyrrhotite is exclusively monoclinic. Monoclinic pyrrhotite from the Brown Face, Mt. Bischoff occurs only in specimens containing concretionary forms of supergene pyrite, and may be the result of supergene modification. Direct formation of monoclinic pyrrhotite at low temperatures appears geologically reasonable in some deposits (e.g. Sawkins et al 1964), but the high formation temperatures for fluorite from fluid inclusion studies indicate that this is not necessary to explain the presence of monoclinic pyrrhotite in the Mt. Bischoff deposit.

Both hexagonal and monoclinic pyrrhotites and mixtures of the two types occur at Mt. Bischoff and the replacement deposits at Renison Bell.

It is probable that the hexagonal pyrrhotite is the 2A, 5C structural type (the stable hexagonal form below the  $\beta$  transformation) if a slow cooling history is accepted, because experimental studies show that pyrrhotites reequilibrate rapidly (e.g. Clark, 1966). The range of composition of the hexagonal pyrrhotites is similar to that shown for the 2A, 5C type by Clark (1966), although several pyrrhotites are slightly S-enriched. It is probable that these pyrrhotites inverted from hexagonal (2A, 7C) pyrrhotites of equivalent composition at the  $\beta$  transformation temperature similarly to the formation of monoclinic pyrrhotite.

However accurate estimates of formation temperatures of the pyrrhotites are restricted by these uncertainties in their formation histories. The following discussion is only valid if it is assumed

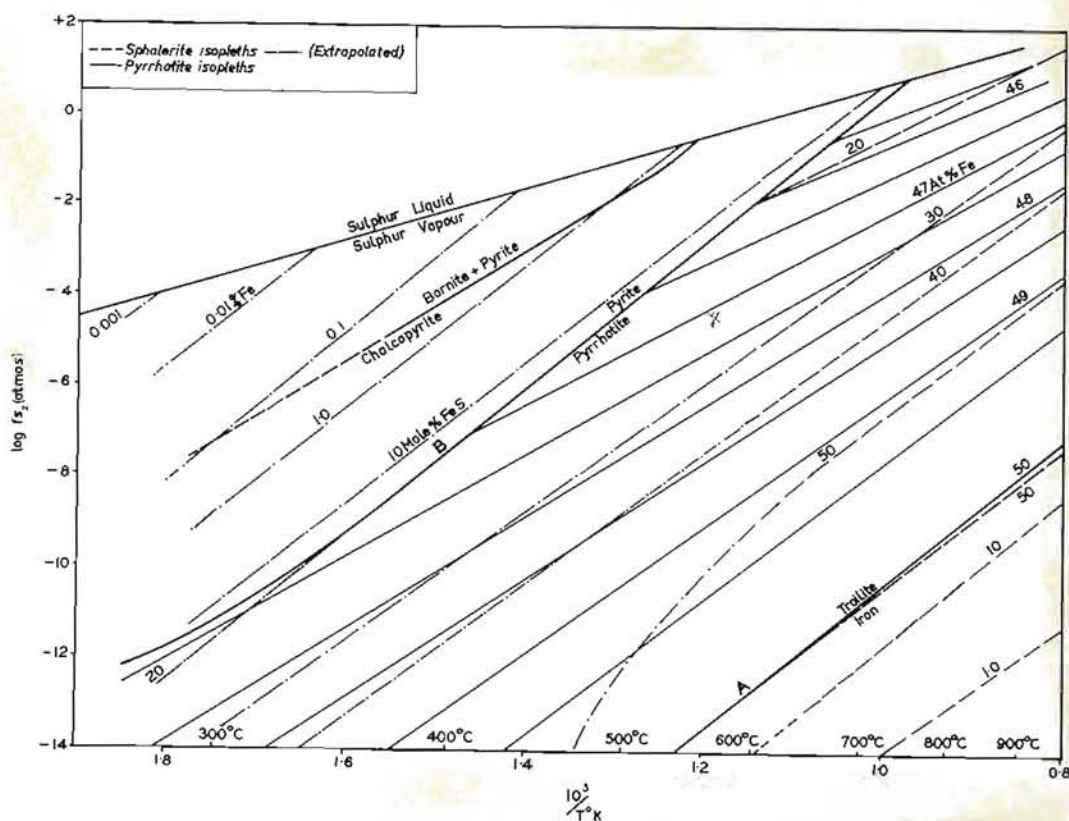


Figure 31. Compositions of pyrrhotite ( in atomic per cent Fe) and sphalerite (in mole per cent FeS) in equilibrium with iron, pyrrhotite or pyrite as a function of fugacity of sulphur and temperature. From Toulmin and Barton (1964) and Barton and Toulmin (1966).

that both the monoclinic and hexagonal (2A, 5C?) pyrrhotite have inverted from hexagonal (2A, 7C) pyrrhotite of equivalent composition during slow cooling.

At Mt. Bischoff the pyrrhotites from the central area (Brown Face - Slaughteryard Face) have predominantly hexagonal symmetry and some are very S-deficient (Fig. 34). Pyrrhotites from Greisen Face, Pig Flat and the south end of the open cut have predominantly monoclinic symmetry and the hexagonal pyrrhotites present are generally more S-rich than those from the Slaughteryard Face.

The minimum temperatures of formation and  $fs_2$  of pyrrhotites from the Slaughteryard and Brown Faces have a continuous range from approximately  $300^{\circ}$  to  $525^{\circ}\text{C}$  and  $10^{-12}$  to  $10^{-3}$  atmospheres respectively. The minimum temperature of formation and  $fs_2$  of pyrrhotites from Greisen Face, Pig Flat and S of Pig Flat generally range from  $400^{\circ}$  to  $525^{\circ}\text{C}$  and  $10^{-5}$  to  $10^{-3}$  atmospheres respectively (Fig. 33) with one exception (100,078a). However textural evidence suggests that the pyrrhotite is not in equilibrium with pyrite and the fluid inclusion studies indicate a temperature gradient from Brown Face-Slaughteryard Face to Greisen-Pig Flat - south of Pig Flat, at least during deposition of the fluorite. If a minimum temperature of  $525^{\circ}\text{C}$  is accepted for some deposition of pyrrhotite in the Greisen Face - Pig Flat area and some deposition at Brown Face - Slaughteryard Face is considered to have occurred at a higher temperature, then if the  $fs_2$  were constant at  $10^{-3}$  atmospheres, a maximum temperature of approximately  $700^{\circ}\text{C}$  is indicated (Fig. 31). The stability fields of pyrite and pyrrhotite at these temperatures

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P139 bound between  
pp 141 or 142

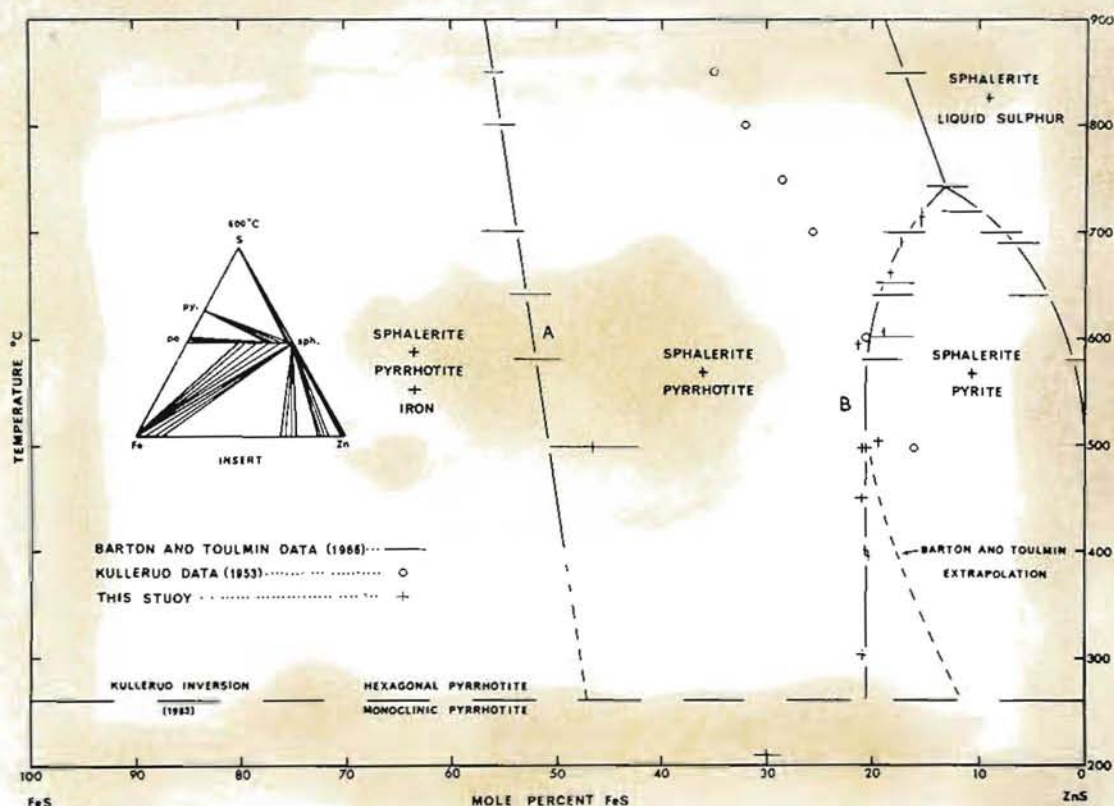


Figure 32. The composition of sphalerite in equilibrium with metallic iron and iron sulphide phases. Diagram from Boorman (1967) and insert after Barton and Toulmin (1966).

indicate a fugacity of oxygen ( $f_{O_2}$ ) between  $10^{-24}$  and  $10^{-17}$  atmospheres, which decreases with decreasing temperature (Holland, 1965). If the  $f_{S_2}$  does not fall rapidly with initial decreasing temperature, conditions would approach and may cross the pyrite-pyrrhotite solvus. This may be the explanation for the increase in abundance of pyrite in the marginal zone at Mt. Bischoff. If the textural evidence that pyrite generally crystallized before pyrrhotite in the replacement deposit is accepted, and sequence of deposition is accepted as being at least partly a function of decline in temperature, it must indicate a higher  $f_{S_2}$  during initial pyrite crystallization, and a maximum initial temperature of  $743^{\circ}\text{C}$ , in the presence of S vapour. The pyrite in the outer zone could be penecontemporaneous with or later than the pyrrhotite and may be equivalent to the second generation pyrite in the replacement deposit. This cannot be confirmed because of the lack of coexisting pyrite and pyrrhotite in specimens from the marginal zone.

Similar minimum temperatures of formation and  $f_{S_2}$  up to  $525^{\circ}\text{C}$  and  $10^{-3}$  atmospheres and  $f_{O_2}$  up to  $10^{-17}$  atmospheres can be demonstrated for the pyrrhotites at Renison Bell and Cleveland. However as no zonal pattern has been determined and no direct temperature measurements made using fluid inclusions, the only indication that the temperature and  $f_{S_2}$  may have been higher is the non-equilibrium textures shown by pyrite and pyrrhotite. The association of monoclinic pyrrhotite and abundant pyrite at Cleveland and Federal Lode, Renison Bell may indicate conditions close to the estimated minimum temperature and  $f_{S_2}$  conditions of  $450^{\circ}$  to  $525^{\circ}\text{C}$  and  $10^{-6}$  to  $10^{-3}$  atmospheres.

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(b) The Fe-Zn-S System

The pioneer work by Kullerud (1953) on the FeS-ZnS join was carried out using techniques in which the fugacity of sulphur was not controlled. Barton and Toulmin (1966) have used the coexistence of pyrite and pyrrhotite as a natural buffer which controls the  $f_{S_2}$  at any given temperature to determine the relationship between the composition of sphalerite, crystallizing in equilibrium with pyrite and pyrrhotite, and the temperature of crystallization (Fig. 31). A major problem encountered by Barton and Toulmin (1966) was that the conditions of formation of sphalerite below  $580^{\circ}\text{C}$  could not be measured directly because of the slow reaction rate of solid state reactions in the system at low temperatures. The slope of their curve relating FeS content of sphalerite in equilibrium with pyrite and pyrrhotite to temperature of crystallization (curve B, Fig. 32) below  $580^{\circ}\text{C}$  indicates that the FeS content of sphalerite in such assemblages is temperature dependent; this was based partly on the observation of systematic variations in sphalerite composition in zoned hydrothermal deposits, and partly as extrapolation of the high temperature data which showed that the FeS content of the sphalerite was a function of the activity of FeS.

Recent studies using salt fluxes to increase the reaction rate (Boorman, 1967) have shown that the sphalerite solvus (curve B, Figs. 33) does not reverse its slope but drops vertically at a constant composition of  $20.8 \pm 0.5$  mole % FeS, i.e. the 20.8 mole % FeS isopleth is coincident with the pyrite-pyrrhotite solvus below  $550^{\circ}\text{C}$  (Fig. 32). The independence of sphalerite composition and temperature of crystallization

below 550°C has also been demonstrated by Scott and Barnes (1967), but Chernyshev and Anfilogov (1967) found a progressive increase in FeS content with decreasing temperature using a similar experimental procedure. Williams (1967) suggested that the FeS content of sphalerite in natural assemblages did not support these experimental studies, and that there was abundant evidence including his own studies at Zeehan and the study of the Salton Sea sulphides (Skinner et al, 1967) to support the extrapolation suggested by Barton and Toulmin (1966). However, there is still considerable uncertainty involved in the interpretation of sphalerite compositions.

The results obtained in this study are shown in Appendix C1 and summarized in Fig. 33B. The sphalerites from the replacement deposit at Mt. Bischoff contain between  $13.8 \pm 1.6$  and  $25.0 \pm 3.8$  mole % FeS and exhibit a generalized decrease in FeS content from Brown Face outwards, although only a few analyses are available. The sphalerites from Brown Face and Slaughteryard Face, which contain more than 20 mole % FeS, are associated with abundant pyrrhotite which from textural relationships was deposited penecontemporaneous with, or slightly before the sphalerite. The sphalerites from Pig Flat and south of Pig Flat have a lower FeS content ( $13.8$  to  $16.0 \pm 3.6$  mole % FeS) but occur predominantly in association with pyrite although some pyrrhotite is present. The sphalerites from the fissure veins, which contain abundant pyrite but only minor pyrrhotite, have a range of composition from  $9.0 \pm 1.8$  to  $17.3 \pm 1.6$  mole % FeS, and there appears to be no relationship between spatial position and composition.



The sphalerite compositions have little thermometric significance when considered alone. It is also evident that estimation of formation conditions is difficult because the sphalerite isopleths are either subparallel or parallel to the pyrite-pyrrhotite solvus and the pyrrhotite isopleths (Fig. 31), and the interpretation of pyrrhotite structure and composition is also uncertain. The compositions of sphalerite from Brown Face-Slaughteryard Face fall entirely within the pyrrhotite field of the FeS-FeS<sub>2</sub> system (Fig. 31) in agreement with observed associations. The overlapping field obtained from the maximum range of compositions of these sphalerites and pyrrhotites (with the assumptions discussed above) indicates temperature and fs<sub>2</sub> conditions between 450°C and 10<sup>-6</sup> atmospheres and 650°C and 10<sup>-2</sup> - 10<sup>-3</sup> atmospheres. The fo<sub>2</sub> at these temperatures would range from 10<sup>-31</sup> to 10<sup>-17</sup> atmospheres. The higher limit of temperature - fs<sub>2</sub> conditions approximate to the conditions indicated by the variations in pyrrhotite compositions alone if a temperature gradient is accepted. The sphalerite compositions from Pig Flat 0 south end of the open cut and from the fissure veins fall entirely within the pyrite field of the FeS-FeS<sub>2</sub> system if Boorman's experimental work is accepted. If Barton and Toulmin's extrapolated curve is considered, only the sphalerites with the highest FeS contents could be in equilibrium with the most Fe-rich pyrrhotites (and possibly pyrite) from Pig Flat. The temperature - fs<sub>2</sub> conditions would be 400°C and 10<sup>-7</sup> atmospheres, significantly lower than the minimum temperature of formation of some pyrrhotites from this area, and lower than the conditions suggested by the distribution of pyrrhotite composition alone. The lower limit of 9 mole % FeS

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recorded for sphalerites in the Waratah district may be significant if the sphalerite isopleths are in fact subparallel or parallel to the pyrite-pyrrhotite solvus in the pyrite field (Fig. 31). It indicates that if the  $fs_2$  was approximately constant, the sphalerites (and pyrites) in the marginal zone of the replacement deposit and fissure veins were deposited over a very small temperature range which was lower than the range of deposition temperatures in the central zone of the replacement deposit, or that if they were deposited at successively lower temperatures, the  $fs_2$  was decreasing sympathetically. Under the latter conditions the  $fo_2$  would also decrease sympathetically. The  $fs_2$  would have had to increase markedly for the temperature of deposition of the sphalerites to have been greater than that for the central zone.

Sphalerites from Cleveland which occur with monoclinic pyrrhotite and replace pyrite, contain between  $14.7 \pm 1.6$  and  $19.7 \pm 1.6$  mole % FeS. The most FeS-rich sphalerite could be in equilibrium with pyrite and pyrrhotite between  $450^\circ\text{C}$  and  $510^\circ\text{C}$  and  $10^{-7}$  to  $10^{-3}$  atmospheres ( $fs_2$ ) and  $10^{-31}$  to  $10^{-17}$  atmospheres ( $fo_2$ ) if the monoclinic pyrrhotite formed from a S-rich hexagonal pyrrhotite by rapid cooling, but the more FeS-deficient sphalerites could not have been in equilibrium with pyrrhotite. If slow cooling is envisaged, with continuous change in the composition of the pyrrhotite until it inverts below the  $\beta$  transformation temperature, then the most FeS-rich sphalerite could have been in equilibrium with pyrite and pyrrhotite from  $510^\circ\text{C}$  down to the transformation temperature ( $\approx 300^\circ\text{C}$ ), and the more FeS-deficient sphalerites could have been in equilibrium with pyrite and pyrrhotite below about  $350^\circ\text{C}$  and  $10^{-10}$

atmospheres ( $fs_2$ ) if Barton and Toulmin's curve is accepted. This would mean that the sphalerite would have been deposited at a significantly lower temperature than the initial temperature of deposition of pyrrhotite.

Sphalerites from the No. 2 Horizon at Renison Bell (4 analyses) contain between  $12.5 \pm 1.6$  and  $21.5 \pm 1.8$  mole % FeS although three of the sphalerites contain above  $17.8 \pm 1.6$  mole % FeS. The maximum temperature -  $fs_2$  conditions for sphalerite of this composition in equilibrium with pyrrhotite of the compositional range at Renison Bell is approximately  $500^\circ\text{C}$  and  $10^{-5}$  atmospheres. The minimum conditions are below  $300^\circ\text{C}$  and  $10^{-11}$  atmospheres ( $fs_2$ ) if Barton and Toulmin's curve is accepted. The overlapping areas formed by the sphalerite and pyrrhotite for Renison Bell fall close to the pyrite - pyrrhotite solvus.

The distribution of FeS contents of sphalerite at Mt. Bischoff can generally be equally well explained using either the experimental curve of Boorman (1967) or the extrapolated curve of Barton and Toulmin (1966). The low FeS contents of sphalerites associated with pyrrhotite at Cleveland may be significant as they are best explained by slow cooling of S-rich hexagonal (2A, 7C) pyrrhotite towards the transformation temperature with deposition of sphalerite in equilibrium with the pyrrhotite below  $350^\circ\text{C}$  if Barton and Toulmin's curve is accepted. Sphalerites intimately associated with pyrrhotite at Renison Bell also have FeS contents below 20 mole % FeS.

The effect of confining pressure may have been partly responsible for the low FeS contents of sphalerites associated with pyrrhotite

obtained in this study. Barton and Toulmin (1966) have shown that the effect of increasing pressure is to move the pyrite-pyrrhotite-sphalerite line (curve B) to the right in Figure 32 (i.e. towards lower FeS contents) and for an increasing effect at lower temperatures (i.e. flattening of curve B, Figure 32). They recorded that the shift was equivalent to -1 mole % FeS per 1000 atmospheres at  $742^{\circ}\text{C}$  increasing to approximately -3 mole % FeS per 1000 atmospheres at  $325^{\circ}\text{C}$ . At Mt. Bischoff, Cleveland and Renison Bell where effective confining pressures probably approached 1000 atmospheres these differences may be significant. It would be possible for 3 of the 4 analysed sphalerites from Renison Bell to have been in equilibrium with hexagonal (2A, 7C) pyrrhotite, and for the analysed sphalerites from Cleveland to more closely approach equilibrium with hexagonal (2A, 7C) pyrrhotite at temperatures in excess of  $350^{\circ}\text{C}$ .

(c) The Fe-As-S System

Clark (1960) has shown that although pyrite is stable up to  $743^{\circ}\text{C}$  and arsenopyrite up to  $702^{\circ}\text{C}$ , the two minerals are not stable as a pair above approximately  $491^{\circ}\text{C}$ , and that if pyrite coexists with arsenopyrite in the presence of vapour at least one member of the mineral pair was deposited below  $491 \pm 12^{\circ}\text{C}$ . This temperature is not affected greatly by the confining pressure or the presence of pyrrhotite coexisting with the arsenopyrite and pyrite.

In the cassiterite-sulphide ores arsenopyrite and pyrite occur as euhedral crystals which are rarely in contact and are commonly apparently replaced by pyrrhotite (Plates 13, 14, 15). Some of the

Figure 33. Variation of parameters of possible thermometric significance with spatial position at Mt. Bischoff and a comparison with the same parameters at Renison Bell and Cleveland.

- A. Formation temperatures of fluorite and quartz from fluid inclusion studies.
  - B. FeS content of sphalerite, expressed as mole %.
  - C. Composition of pyrrhotite, expressed as atomic % Fe.
  - D. Isotopic composition of sulphur, expressed as  $\delta^{34}\text{S}$ .
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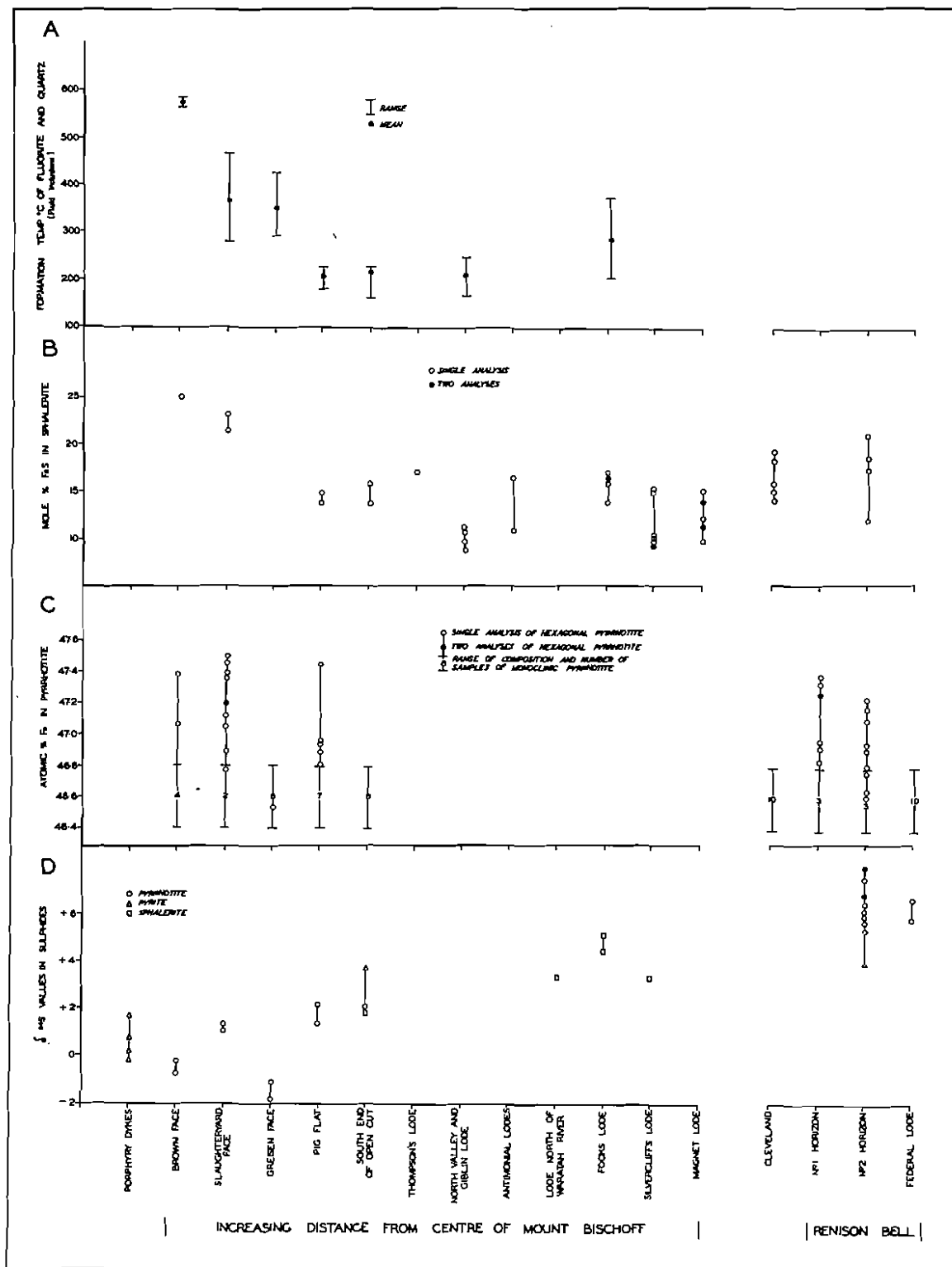


Figure 33

pyrrhotite has a probable minimum temperature of  $525^{\circ}\text{C}$  and actual temperatures of deposition may have approached  $700^{\circ}\text{C}$  at Brown Face and Slaughteryard Face where temperatures of deposition of fluorite (which on textural evidence is generally deposited after pyrite and arsenopyrite) were as high as  $590^{\circ}\text{C}$  and  $470^{\circ}$  respectively.

This evidence suggests that the pyrite and arsenopyrite probably formed above  $491^{\circ}\text{C}$ . Possible explanations to explain this apparent anomaly are: (a) that the pyrite and arsenopyrite did not coexist with vapour; this is also suggested by their general separation in the ores, (b) the effect of other components on the pyrite-arsenopyrite stability, although Clark (1960) recorded that the presence of water had little effect, (c) the textural relationships are not the result of successive deposition (e.g. Stanton, 1964), although it is difficult to explain some configurations (e.g. Plate 14) as growth textures.

The problem is also complicated by the compositions of the arsenopyrites as indicated by measurements of their 131 spacing (Clark, 1960). Arsenopyrites from the Slaughteryard Face, Mt. Bischoff and Federal Lode and No. 2 Horizon, Renison Bell have a narrow compositional range between 36.5 and 37.5 atomic percent S (Morimoto and Clark, 1961). Clark (1960) has shown that the composition of arsenopyrite is temperature dependent, and by extrapolation of his results arsenopyrites of this compositional range would have been formed at approximately  $300^{\circ}\text{C}$  under low pressure conditions. Increasing pressure results in increased sulphur content in the arsenopyrites. However using the maximum range of calculated pressures and the pressure dependent compositional variations

quoted by Clark (1960) the arsenopyrites should still have formed below 500°C, and probably as low as 375°C if estimates are correct. Hence estimates of temperature within the Fe-As-S system are consistent but are generally lower than estimates based on other systems, if the textural evidence for successive deposition is accepted. Similar studies by Arnold, Coleman and Fryklund (1962) on ores from the Coeur d'Alene District, Idaho have indicated minimum temperatures of formation of pyrrhotite up to approximately 490°C in sections containing pyrite and arsenopyrite; both minerals were generally deposited before pyrrhotite.

(d) Pyrite Geothermometer

Hill and Green (1962) have related the thermoelectric potential of pyrites from Mt. Bischoff and Renison Bell to temperatures of formation as suggested by Smith (1947). Low resistivities (positive thermoelectric potentials) were obtained for both groups of pyrites and were related to high temperatures of formation. Slightly lower resistivities were obtained for pyrite at Mt. Bischoff than at Renison Bell, and a higher temperature of deposition was suggested. Some local correlation between resistivity and Cu and/or Mo content was suggested on the basis of 5 analyses of pyrite, but the analyses do not justify this correlation.

It is now evident that the trace or minor element content of the pyrite is the principal factor governing the thermoelectric potential (e.g. Suzuki, 1963), and that this is probably a function of the nature of the ore-forming fluid. The similar positive thermoelectric potential of pyrites from Mt. Bischoff and Renison Bell may be a function of their similar trace element content. This is partly substantiated by the

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similar, low Co and Ni contents of pyrites from these deposits (Loftus-Hills, 1967).

(e) Melting Points and Solid Solutions

Melting points of minerals place an upper limit to the temperature range in which the mineral formed. The occurrence of native bismuth associated with galena at Renison Bell is useful as it limits the temperature of this phase of mineralization to below  $271^{\circ}\text{C}$  (e.g. Edwards, 1954, p. 150). At  $250^{\circ}\text{C}$  the  $\text{fo}_2$  and  $\text{fs}_2$  conditions during deposition of this mineral pair are limited by the stability of native bismuth. The  $\text{fs}_2$  and  $\text{fo}_2$  must have been below  $10^{-14}$  and  $10^{-32}$  atmospheres respectively (Holland, 1965).

Temperatures of homogenization of sulphide exsolution intergrowths (e.g. Edwards, 1954, p. 92) may be used as indicators of minimum temperatures of formation. However they must be treated with caution because of the difficulty of accurately delimiting the exsolution textures (e.g. Brett, 1964) and the relatively short times employed in homogenization. Homogenization temperatures for the exsolution pairs identified in the cassiterite-sulphide ores (Table 9) are not inconsistent with temperatures determined from compositions of pyrrhotite and sphalerite and observed sequence of deposition, and are at least indicative of high temperatures prevailing during deposition of pyrrhotite, chalcopyrite, sphalerite and stannite.

<u>Solvent</u>	<u>Solute</u>	<u>Homogenization Temperature</u>
Sphalerite	Chalcopyrite	350 - 400°C
Chalcopyrite	Sphalerite	550°C
Chalcopyrite	Pyrrhotite	600°C
Stannite	Chalcopyrite	500°C

Table 9. Homogenization temperatures for exsolution pairs  
(Edwards, 1954).

### Sulphur Isotopes

A number of isotope analyses of sulphides from Mt. Bischoff and Renison Bell have been recorded by Rafter and Solomon (1967). The results are tabulated in Appendix C2 and summarized in Figure 33D.

At Mt. Bischoff the  $\delta^{34}\text{S}$  values for sulphides from the dykes and the central area of the replacement deposit are close to zero (-0.7 to +1.7) but those from the marginal zone of the replacement deposit are slightly enriched in  $\delta^{34}\text{S}$  (+1.4 to 3.8). A local reversal is shown by sulphides from the Greisen Face which have  $\delta^{34}\text{S}$  values of -1.1 and -1.9. The sulphides from the marginal fissure veins are also enriched in  $^{34}\text{S}$  ( $\delta^{34}\text{S} = +3.4$  to  $+5.2$ ) relative to sulphides from the central zone. Rafter and Solomon (1967) have suggested two mechanisms to explain this variation. They suggested that at the high temperatures prevailing in the central zone sulphur isotope fractionation would be small but could result in the early sulphides (derived from relatively abundant  $\text{H}_2\text{S}$ ) being very slightly enriched in  $^{32}\text{S}$  (e.g. Smitheringale and Jensen, 1963). Later sulphides deposited at

probably lower temperatures would then derive sulphur from a reservoir slightly depleted in  $^{32}\text{S}$ . Alternatively they suggested the more attractive hypothesis that the mass isotope effect would trend towards initial preferential deposition of  $^{32}\text{S}$  which could again result in a residual reservoir depleted in  $^{32}\text{S}$ . Rafter and Solomon (1967) pointed out that these processes would explain the  $\delta^{34}\text{S}$  trends if a supply of a uniform ore fluid was operative, but that part of the observed variation could be the result of compositional changes in sulphur of the ore fluid with time. This may explain the anomalous similarity of  $\delta^{34}\text{S}$  values of sulphides from Fook's Lode to values of sulphides from other marginal lodes when a local source of ore fluids is indicated by a combination of high formation temperature, high salinity and high Na/K ratios of fluid inclusions in fluorite from Fook's Lode.

It is interesting that the variation in  $\delta^{34}\text{S}$  is the opposite to that shown at Zeehan, where  $\delta^{34}\text{S}$  shows a decline with increasing distance from the probable source region (Both, Rafter and Solomon, 1967).

Sulphur isotope analyses from Renison Bell involved sulphides from many environments including the conformable replacement deposits, the Federal Lode, and from disseminated sulphides in the Renison Bell Shales. The  $\delta^{34}\text{S}$  values for Fe- sulphides range from +4.0 to +8.1 (average +6.5) and a single galena sample gave +2.2. There is apparently no significant variation within or between deposits. The sulphur is even heavier than that from sulphides in the outer fissure veins at Mt. Bischoff. Rafter and Solomon (1967) pointed out that the Renison Bell deposits were considerably further from the apparent

granitic source rocks than at Mt. Bischoff where increasing distance from the centre of mineralization appears to correlate with heavier sulphur. However a similar distance from the source is indicated by equivalent temperatures of deposition to at least the marginal replacement deposit at Mt. Bischoff and the difference may represent an initial difference in sulphur for the local granitic source. For example the  $\delta^{34}\text{S}$  values of sulphides in the Heemskirk Granite range from +2.2 to +15.1 (Both, Rafter and Solomon, 1967) and in the Mt. Bischoff porphyries they are significantly lower and range from -0.2 to +1.7.

#### Trace Elements

Analyses of Co and Ni in Fe sulphides at Mt. Bischoff and Renison Bell have been carried out by G. Loftus-Hills and the author, using the analytical technique described by Loftus-Hills and Solomon (1967). The study was designed to determine whether the variation in other parameters at Mt. Bischoff was reflected in the Co and Ni content of the Fe sulphides. Although it is evident that the concentrations of the elements should not be purely temperature-dependent due to their undersaturation in the sulphides, some examples of trace element zoning have been recorded (e.g. Rose, 1967).

Examination of pyrrhotite, pyrite and arsenopyrite from within an area of 10 sq. ins. of the Slaughteryard Face (Table 10, Fig. 35) indicates that the pyrite contains significantly more Co and Ni than the pyrrhotite and that the arsenopyrite shows considerable enrichment in Co

Locality	Mineral Analyses	No. of	Range (ppm)		Mean (ppm)		Co/Ni
			Co	Ni	Co	Ni	
MT. BISCHOFF							
White Face Dyke	po.	2	0-11	14-74	6	44	0.14
White Face	py.	12	1-6	8-28	3.5	13	<u>0.26</u>
North-eastern Dyke	py.	10	1-5	5-25	3.5	12	<u>0.28</u>
Brown Face Dyke	po.	2	10-13	11-13	12	12	1.00
Vein in Brown Face Dyke	py.	2	10-11	46-51	10	49	<u>0.20</u>
Vein in White Face Dyke	py.	1	-	-	13	8	<u>1.65</u>
Brown Face	po.	6	1-20	5-11	8	8	1.00
Slaughteryard Face	po.	6	1-21	2-15	6	8	0.75
	py.	2	7-8	4-47	8	26	<u>0.31</u>
	apy.	2	107-114	7-13	111	10	11.1
	py. (sec)	3	6-16	17-42	9.5	30	<u>0.31</u>
Greisen Face	po.	5	9-29	5-28	19	13	1.46
Pig Flat	po.	6	1-11	5-26	4.5	12	0.38
S. end of open cut	py.	4	1-16	5-13	9	9	<u>1.00</u>
Happy Valley	po.	3	1-2	11-25	2	16	0.13
	py.	4	2-13, 210	16-44	61	31	<u>1.97</u>
Veins below Brown Face	po.	3	2-22	56-82	9	71	0.13
	apy.	2	207-209	134-137	208	136	1.53
	py.	2	14-18	26-28	16	27	<u>0.58</u>
Vein beneath Greisen Face	po.	4	5-9	71-109	7	90	0.08

Locality	Mineral Analyses	No. of	Range (ppm)		Mean (ppm)		Co/Ni
			Co	Ni	Co	Ni	
Giblin Lode	py.	2	73-82	142-168	78	155	<u>0.50</u>
Vein near Don Hill	py.	2	4-5	15	5	15	<u>0.33</u>
North Valley Lode	py.	4	7-100	34-82	47	64	<u>0.73</u>
Antimonial Lode	py.	3	2-3	4-9	3	7	<u>0.36</u>
Lode N. of Waratah River	py.	1	-	-	2	16	<u>0.12</u>
Fooks Lode	py.	4	2-70	13-103	28	45	<u>0.62</u>
RENISON BELL							
Veins, Battery Open Cut	py.	10	1-16	12-91	8	34	<u>0.24</u>
Replacement of siltstone	py.	8	0-10	2-33	4	18	<u>0.22</u>
Battery Open Cut							
No. 1 Horizon	po.	8	0-10	11-18	4	14	0.29
	py.	4	23-53	25-52	35	39	<u>0.90</u>
No. 2 Horizon	po.	9	3-53	3-19	16	10	1.60
	py.	4	65-139	28-46	119	38	<u>3.13</u>
	apy.	1	-	-	103	5	20.60
Federal Lode	po.	9	7-62	57-111	22	92	0.24

Table 10. Cobalt and nickel contents of iron sulphides from

Mr. Bischoff and Renison Bell. Analysed by G. Loftus-Hills, 1966-68 and D. Groves and W. Baker, 1968.

po - pyrrhotite; py - pyrite; apy - arsenopyrite;

sec. - secondary.

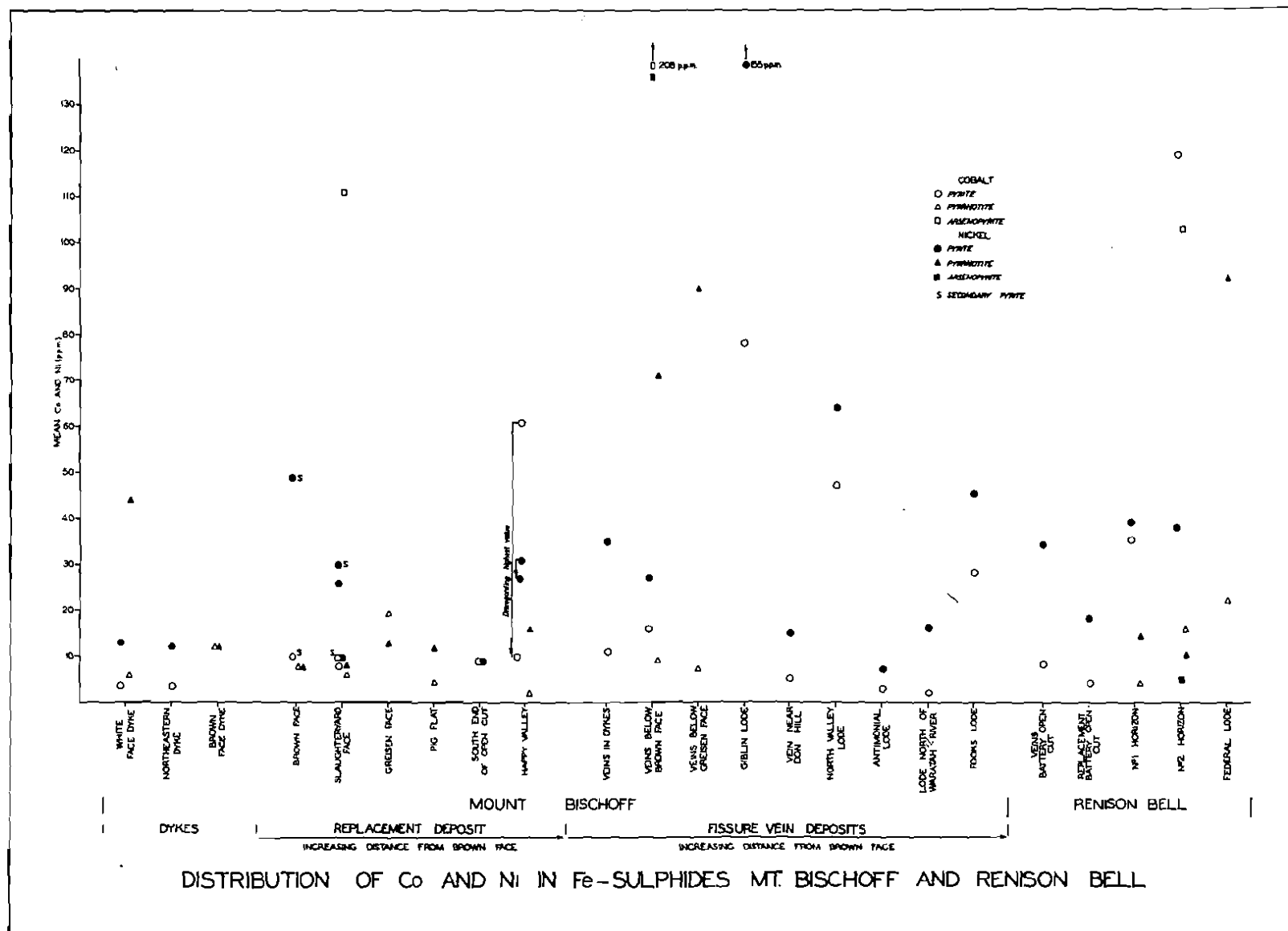
(see also Gavelin and Gabrielson, 1947; Fleischer, 1955). On a broader scale, pyrites from Happy Valley Face also exhibit Co and Ni enrichment with respect to pyrrhotite from the same area. It has generally been found that Co is enriched preferentially in pyrite and that Ni is enriched in pyrrhotite (e.g. Neumann, 1950; Hawley and Nichol, 1961). The unusual enrichment of Ni in pyrite relative to pyrrhotite at Mt. Bischoff is probably a result of disequilibrium between the two minerals, which is also indicated by textural relationships.

The Co and Ni analyses do not indicate a simple spatial relationship related to zoning either in the replacement deposit or vein deposits (Fig. 34). A possible trend is indicated by higher mean Ni and lower mean Co in pyrrhotites from the outer zone of the replacement deposit (Fig Flat, Happy Valley) than in pyrrhotites from the central zone (Brown Face, Slaughteryard Face), but the pyrrhotites from the intermediate area (Greisen Face) have higher mean Co than Ni and therefore disrupt this trend.

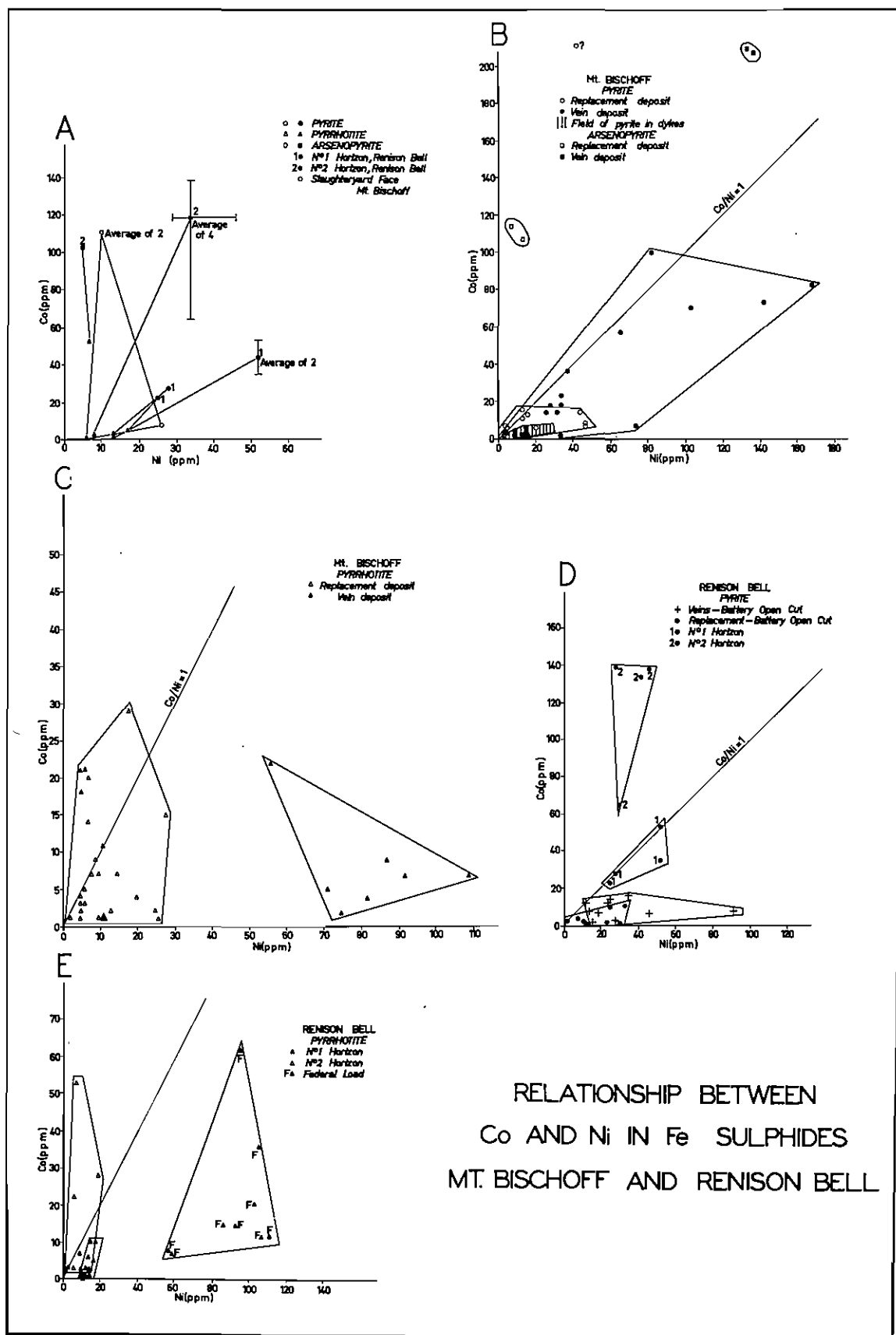
There are however major differences in Co and Ni contents of pyrrhotite pyrite and arsenopyrite between the replacement deposits and the veins (Fig. 35). Pyrrhotites from the vein deposits have a similar range of Co contents to pyrrhotites from the replacement deposits but are markedly enriched with respect to Ni. Although the Co and Ni contents of pyrites from the vein deposits and replacement deposits partly overlap, their distribution can be shown to be significantly different at the 92% level of confidence (unbiased two-variable multivariant analysis), and it is evident that the pyrites from the vein deposits are enriched in both Co and Ni. Pyrites from the porphyry dykes show an

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Figure 35







RELATIONSHIP BETWEEN  
Co AND Ni IN Fe SULPHIDES  
MT. BISCHOFF AND RENISON BELL

Figure 35

even more restricted range of Co and Ni contents than pyrites from the replacement deposits. Two analyses of arsenopyrite from the vein deposits indicate that it is enriched in both Co and Ni relative to arsenopyrite from a replacement deposit in porphyry; there is almost a fourteen-fold enrichment in Ni. Hence there is a greater variation in Co and Ni contents with an overall enrichment in pyrrhotite, pyrite and arsenopyrite from the vein deposits relative to the replacement deposits, with a preferential enrichment in Ni.

This difference may result from changes in the ore-forming fluid prior to vein formation or from differences in the conditions of deposition in the two environments. The relatively small variation in Co and Ni in the replacement deposits may reflect stabilization of the physico-chemical conditions of the ore-forming fluids due to the large effect of the dolomitic host rocks. Rose (1967) also recorded a greater variation in trace elements in vein deposits than in replacement deposits in part of southern U.S.A.

At Renison Bell the distribution of Co and Ni between pyrrhotite and pyrite in the replacement deposits is similar to that at Mt. Bischoff. The pyrites exhibit strong enrichment in Co and Ni, but there are proportional variations in Co and Ni for pyrite-pyrrhotite pairs (Fig. 35).

The Co and Ni contents of penecontemporaneous pyrite veins and pyrite replacement of siltstones in the Battery open cut overlap (Fig. 35) but are significantly different at the 94% confidence level. There is both Co and Ni enrichment in the vein pyrites, with preferential enrichment in Ni, and in this respect the differences between the veins

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and replacement is similar to that at Mt. Bischoff. The apparent difference between Co and Ni contents of pyrites from No. 2 Horizon and No. 1 Horizon, cannot be substantiated as they only represent one and two specimens respectively. The Co and Ni contents of pyrrhotites from No. 1 and No. 2 Horizons overlap but are significantly different at the 92% confidence level, with the pyrrhotite from No. 2 Horizon showing a tendency to be enriched in Co. However, both groups of pyrrhotites have low Ni contents (<20 ppm). Pyrrhotites from the Federal Lode have a similar range of Co contents to pyrrhotites from the No. 2 Horizon, although their mean Co content is slightly higher. However, the pyrrhotites from the Federal Lode are strongly Ni-enriched relative to pyrrhotite from both No. 1 and No. 2 Horizons, and in this respect are similar to pyrrhotites from vein deposits at Mt. Bischoff. This preferential enrichment in Ni provides empirical support for the Federal Lode being at least in part a vein deposit.

The constant preferential Ni enrichment in Fe-sulphides from vein deposits relative to replacement deposits at Mt. Bischoff and Renison Bell suggests that the difference between deposits results from the existence of different conditions of deposition between the two environments rather than from a temporal variation. It is possible that in the replacement deposits, Ni, and to a lesser extent Co, have preferentially entered suitable silicate and/or carbonate structures that were not present during vein deposition.

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